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SOLID STATE COOLING WITH ADVANCED OXIDE MATERIALS

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Final Report

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14. ABSTRACT

The major discoveries of the program include: 1) discovery of high-performance materials based on compositionally-graded materials with figures of merit 3-12-times larger than traditional materials; 2) study of candidate high-performance materials possessing strong lattice-polarization coupling and electric-field response and insights into how strain can be used to deterministically tune important parameters; 3) quantification of intrinsic, extrinsic, and secondary contributions to thermal response of polydomain films; 4) quantification of elastocaloric effects in materials that cause the total pyroelectric and electrocaloric coefficients to be different and is related to the piezoelectric effect which causes a lattice expansion which subsequently lowers the frequencies of the lattice vibrations and, in turn, increase the vibrational entropy; 5) development novel, microfabrication-based platforms which provide multi-dimensional control and manipulation of materials. Based on our measurements we conclude that minimizing the resistive heating in these thin films is critical for electrocaloric refrigeration applications.

15. SUBJECT TERMS
electrocaloric; thin-film; complex oxides; pyroelectric; solid state cooling

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Solid State Cooling with Advanced Oxide Materials

Grant AF FA 9550-11-1-0073

Lane W. Martin, David G. Cahill, and William P. King

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Program Overview

The focus of this program was to probe electro-(magneto-)caloric materials for solid state cooling. As part of our work, we aimed to address gaps in the understanding of how to control and exploit these effects for real engineering systems by developing theoretical and experimental approaches to study thermodynamic properties and effects in thin film systems. Despite considerable interest in these topics, a number of factors have limited the development of electrocaloric materials for practical applications including limited pathways to tune properties in these materials, a pressing need to identify new ways of enhancing performance (or limiting losses) in electrocaloric materials, imprecise testing methods (which have produced fundamental questions over the validity of studies), and limits to the magnitude of electric (magnetic) fields that can be applied to bulk samples. The Program aims to overcome these challenges by producing a comprehensive approach that combines design, synthesis, and characterization of thin film oxides (something called for by researchers in the field), a focus on assessing (un)common losses and limiting effects in these materials, and the exploration of new materials and routes to enhance field-induce entropic effects. As part of this, we worked to develop methodologies to directly probe and distill the fundamental response of these materials in operation. In essence we asked the question of how does one produce large field-driven entropic changes in materials. All told, the program combined phenomenological modeling, advanced materials synthesis, and new measurement techniques to understand the fundamental materials science and engineering of solid state cooling materials. The program has run from June 1, 2011 to May 31, 2014 and has supported 2 graduate student researchers (spread across the three PIs). During the duration of the program, we have had three Program Managers. The program was started under Dr. Kumar Jata before being transferred to Dr. Joan Fuller who administered the first year review. From there the program was transferred to Dr. Ali Sayir who has served as the cognizant Program Manager since that time.

Program Highlights

The major discoveries of the program include:

1) The discovery and validation of novel, high-performance cooling materials based on compositionally-graded versions of materials that possess figures of merit of solid state cooling 3-12-times larger than traditional materials. This includes the development of phenomenological models to support this work.
2) The synthesis and study of other candidate high-performance materials possessing strong lattice-polarization coupling and electric-field response. Fundamental insights into how strain and residual strain in materials can be used to deterministically tune the parameters important for electrocaloric cooling were completed.
3) New understanding of intrinsic (arising from temperature-driven changes in polarization), extrinsic (arising from the temperature-dependent motion of domain walls), and secondary (arising from thermal expansion mismatch between the film and the substrate) contributions to thermal response in realistic polydomain films was obtained. This includes the development of the first phenomenological models

to include all three effects, measurements aimed a separating the effects, and demonstration of deterministic control of these effects to produce high-performance materials.

4) Identification and quantification of elastocaloric effects in materials. This previously underappreciated potential loss or reduction of performance in these materials was probed by directly measuring both the polarization change with temperature (*dP/dT*) and the entropy change with temperature (*dS/dE*). It is observed that both the total pyroelectric and electrocaloric coefficients are not the same and that the difference simplifies to a product of the piezoelectric coefficient, the elastic constant, and the coefficient of thermal expansion. We propose that the piezoelectric effect causes a lattice expansion which subsequently lowers the frequencies of the lattice vibrations and, in turn, increase the vibrational entropy. This effect is called the elastocaloric effect and, in this case, opposes the electrocaloric effect.
5) Development novel, microfabrication-based platforms to characterize the electrocaloric temperature change in nanometer-scale thin films. These microfabricated platforms provides independent control of the out-of-plane electric field across the active electrocaloric film while simultaneously allowing measurement of the resulting temperature change from the corresponding resistance change of the electrically isolated metal strip thermometer. The superimposition of the periodic electric field across the film thickness and sensing voltage along the thermometer strip at different frequencies results in an electrocaloric temperature change at the sum and difference of these two frequencies which is measured using a lock-in amplifier. Based on our measurements on multiple films with varying electrical resistivity we conclude that minimizing the resistive heating in these thin films is critical for electrocaloric refrigeration applications.

Program Discoveries and Details

Overview. The work of the team can be broken down into three major areas over the previous three years: 1) design, discovery, and validation of new high-performance materials, 2) advances in new understanding and insight as to the fundamental thermal response of these materials, and 3) development of novel measurement techniques and devices to enable testing and understanding of these materials. In the following we will highlight aspects of each. The summary ends with a list of publications and presentations made by the team during the duration of the project.

New high-performance materials. As part of this program we have probed a new class of materials – name compositionally-graded thin films – that possess a unique combination of physical properties that drives the figure-of-merit for electrocaloric cooling and pyroelectric energy conversion beyond what has been observed previously. In particular, we have observed dramatically reduced dielectric and robust ferroelectric and pyroelectric properties in compositionally-graded versions of $PbZr_{1-x}Ti_xO_3$. The combination of properties – typically unobtainable in materials – results from the formation of a built-in electric fields in the material which develops due to the strain gradient induced by the compositional gradient that turns on a so-called flexoelectric effect. This built in potential gives rise to ferroelectric hysteresis loops that are shifted along the voltage axis (thus possessing two different zero-field stable states with the same net polarization) and also quenches the extrinsic permittivity from ferroelectric domain walls thereby reducing the overall permittivity. Such compositionally-graded heterostructures also possess ferroelectric domain structures that are largely determined by the structural evolution at the film-substrate interface and exotic domain structures that are not found in single layer versions of these materials. We have also developed phenomenological models to address the coupling of the mechanics of the strain-gradient with the polarization to being to predict the evolution of properties in these materials. Furthermore, we have probed the potential of these materials for a range of thermal applications – including electrocaloric cooling, pyroelectric energy conversion, thermal imaging, and more. In general, the figures of merit for such applications are proportional to the pyroelectric coefficient (or the pyroelectric coefficient squared) and inversely proportional to the dielectric permittivity. In this context, the observation of large pyroelectric effects, but diminished permittivity means that the compositionally-graded films have dramatically enhanced figures of merit which are 3−12 times larger than the currently used, standard materials $LiNbO_3$

and $LiTaO_3$. This work has resulted in three publications: 1) R. V. K. Mangalam, *et al.*, *Adv. Mater.* **25**, 1761 (2013), 2) J. Karthik, *et al.*, *Phys. Rev. B* **87**, 024111 (2013), and 3) R. V. K. Mangalam, *et al.*, *ACS Appl. Mater. Interfaces* **5**, 13235 (2013).

Additionally, we have also probed other candidate systems which potential for large electrocaloric response including the morphotropic phase boundary composition of the $PbZr_{1-x}Ti_xO_3$ system (*i.e.*, $PbZr_{0.52}Ti_{0.48}O_3$) which has the potential to possess large field-induced entropic effects due to a strong polarization-lattice coupling. In this regard, we have produced arguably the best thin-film samples of this materials ever produced. Despite extensive work on this material, relative few studies have explored the effect of epitaxial strain on $PbZr_{0.52}Ti_{0.48}O_3$. We explored how epitaxial strain impacts the structure and properties of films of this material. Thin films were found to possess "relaxed" or nearly "relaxed" structures despite growth on a range of substrates. Subsequent studies of the dielectric and ferroelectric properties reveal films with low leakage currents facilitating the measurement of low-loss hysteresis loops down to measurement frequencies of 30 mHz and dielectric response at background dc bias fields as large as 850 kV/cm. Despite a seeming insensitivity of the crystal structure to the epitaxial strain, the polarization and switching characteristics are found to vary with substrate. The elastic constraint from the substrate produces residual strains that dramatically alter the electric-field response including quenching domain wall contributions to the dielectric permittivity and suppressing field-induced structural reorientation. These results demonstrate that substrate mediated epitaxial strain of $PbZr_{0.52}Ti_{0.48}O_3$ is more complex than in conventional ferroelectrics with discretely defined phases, yet can have a marked effect on the material and its responses. This work provided an ideal system for further study of electrocaloric potential. This work was published in J. C. Agar, *et al.*, *Adv. Mater. Interfaces* (DOI: 10.1002/admi.201400098).

New understanding of thermal responses. As part of this program we have also developed fundamental new insights as to the thermal response of materials. For instance, using the tetragonal ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ as a model system, we extensively probed the role of domain structures in controlling the thermal response of these materials. This includes the development of the first phenomenological models to include intrinsic (arising from the change in polarization with temperature in a material), extrinsic (arising from the temperature-dependent motion of domain walls), and secondary (arising from thermal expansion mismatch between the film and the substrate) contributions to thermal response in realistic polydomain films. These predictions suggest significant extrinsic contributions and potentially large secondary contributions to the overall response. Subsequent measurement of model thin films controlled to have different densities of domain walls revealed, for the first time, a dramatic increase in the thermal response as the fraction of in-plane oriented domains increased and how thermal expansion mismatch with the substrate can change the response. These studies beget additional laser-based probes of these effects aimed at understanding the relative roles of primary (intrinsic + extrinsic) and secondary effects. This new method (described in detail below) allows for the separation and quantification of both primary and secondary contributions to thermal response as a function of electric field. By modulating the laser as the heat source in the frequency range 1 Hz to 10 MHz we probed the primary and secondary response of $Ba_{0.6}Sr_{0.4}TiO_3$ and $PbZr_{0.2}Ti_{0.8}O_3$ as a function of applied electric field for films grown on a range of substrates. The secondary contribution to the thermal response, again caused by in-plane thermal expansion mismatch and the piezoelectric nature of the materials, can be quantified by studies at low- and high-frequencies. The secondary pyroelectric effect has the same dependence on applied field as the pyroelectric coefficient and is approximately 15% and 20% of the total response for $PbZr_{0.2}Ti_{0.8}O_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$, respectively. This work has been published in J. Karthik, *et al.*, *Phys. Rev. Lett.* **109**, 257602 (2012) and T. Trong, *et al.*, in preparation May 2014.

Another new insight made possible by this program focuses on the so-called elastocaloric effect in materials and this previously underappreciated potential loss or reduction of performance in these materials. Again, probing the $PbZr_{0.2}Ti_{0.8}O_3$ films as a model system, our laser-based methods have enabled us to probe – for the first time – both the polarization change with temperature (*dP/dT*) and the entropy change with temperature (*dS/dE*). In turn, we can extra both the total pyroelectric Π and electrocaloric Σ coefficients

with high frequency thermal and electric fields. At high frequencies, the in-plane strain is constant and we show that the difference Π-Σ simplifies to a product of the piezoelectric coefficient, the elastic constant, and the coefficient of thermal expansion. We propose that the piezoelectric effect causes a lattice expansion which subsequently lowers the frequencies of the lattice vibrations and, in turn, increase the vibrational entropy. This effect is called the elastocaloric effect and, in this case, opposes the electrocaloric effect. This work highlights a new contribution that must be accounted for and provides guidance to the future design of new materials. This work is summarized in the publication T. Trong, *et al.*, under review *Phys. Rev. Lett.* May 2014.

New probes and devices based on electrocalorics. The last area this program has impacted is the development of novel probes of thermal response in ferroic materials. As part of this program we have developed laser-based direct measurements of both the pyroelectric and electrocaloric effects as a function of temperature, electric field strength, and frequency. Using modern ultrafast pump-probe geometries we can 1) excite capacitor structures with laser energy (heat) and probe the resulting pyroelectric current produced or 2) excite capacitor structures with an applied electric field and probe the temperature change in the capacitor using temperature-dependent reflectance measurements of the top metal. By changing the laser frequency and power we can change the thermal penetration depth and temperature change. With such techniques we can separate primary (intrinsic + extrinsic) pyroelectric and electrocaloric responses from secondary contributions (arising from changes in polarization from thermal expansion combined with the piezoelectric effect) and can unique probe *dP/dT* and *dS/dE* in a direct manner.

At the same time, we have developed novel, microfabrication-based platforms to characterize the electrocaloric temperature change in nanometer-scale thin films. The devices includes high-quality complex oxide films with epitaxial $SrRuO_3$ electrodes deposited on a single crystal substrates. This microfabricated platform provides independent control of the out-of-plane electric field across the active electrocaloric film while simultaneously allowing measurement of the resulting temperature change from the corresponding resistance change of the electrically isolated metal strip thermometer. The superimposition of the periodic electric field across the film thickness and sensing voltage along the thermometer strip at different frequencies results in an electrocaloric temperature change at the sum and difference of these two frequencies which is measured using a lock-in amplifier. The measured voltage is used to estimate the temperature change by characterizing the temperature coefficient of resistance (TCR) of the metal temperature sensor. The measured temperature change is a function of the applied field frequency. Higher frequency operation confines heat spreading and results in higher measured temperature changes. The adiabatic electrocaloric temperature change can be estimated by extrapolating to high frequencies where practically no heat spreading takes place. In addition to the direct temperature change measurement, we also developed a frequency-domain analytical model that allowed us to investigate the electric field as well as frequency dependence of the measured temperature change. This model included the contribution from Joule heating of the thin film due to resistive leakage which counteracts the electrocaloric temperature change. Based on our measurements on multiple films with varying electrical resistivity we conclude that minimizing the resistive heating in these thin films is critical for electrocaloric refrigeration applications.

Publications

1. T. Tong, J. Karthik, L. W. Martin, D. G. Cahill, Secondary effects in wide frequency range measurements of the pyroelectric coefficient of $Ba_{0.6}Sr_{0.4}TiO_3$ and $PbZr_{0.2}Ti_{0.8}O_3$ epitaxial layers, in preparation May 2014.
2. R. Xu, J. Zhang, Z.-H. Chen, J. Karthik, L. W. Martin, Orientation dependent structural phase diagrams and dielectric properties of $PbZr_{1-x}Ti_xO_3$ Part I. monodomain thin films, under review at *Phys. Rev. B* May 2014.
3. T. Tong, J. Karthik, R. V. K. Mangalam, L. W. Martin, D. G. Cahill, Reduction of the electrocaloric entropy change of ferroelectric $PbZr_{1-x}Ti_xO_3$ epitaxial layers due to an elastocaloric effect, under review at *Phys. Rev. Lett.* May 2014.

4. J. Z. Zhang, R. Xu, A. R. Damodaran, Z.-H. Chen, L. W. Martin, Understanding order in compositionally-graded ferroelectrics: flexoelectricity, gradient, and depolarization field effects, accepted *Phys. Rev. B* May 2014.
5. J. C. Agar, R. V. K. Mangalam, A. R. Damodaran, G. Velarde, J. Karthik, M. B. Okatan, Z. H. Chen, S. Jesse, N. Balke, S. V. Kalinin, L. W. Martin, Tuning susceptibility via misfit strain in relaxed morphotropic phase boundary $PbZr_{1-x}Ti_xO_3$ epitaxial thin films, *Adv. Mater. Interfaces* (2014). (DOI: 10.1002/admi.201400098).
6. R. V. K. Mangalam, J. C. Agar, A. R. Damodaran, J. Karthik, L. W. Martin, Improved pyroelectric figures of merit in compositionally graded $PbZr_{1-x}Ti_xO_3$ thin films, *ACS Appl. Mater. Interfaces* **5**, 13235 (2013).
7. R. V. K. Mangalam, J. Karthik, A. R. Damodaran, J. C. Agar, L. W. Martin, Unexpected crystal and domain structure and properties in compositionally graded $PbZr_{1-x}Ti_xO_3$ thin films, *Adv. Mater.* **25**, 1761 (2013).
8. J. Karthik, R. V. K. Mangalam, J. C. Agar, L. W. Martin, Large built-in electric fields due to flexoelectricity in compositionally graded ferroelectric thin films, *Phys. Rev. B* **87**, 024111 (2013).
9. J. Karthik, J. C. Agar, A. R. Damodaran, L. W. Martin, Effect of 90° domain walls and thermal expansion mismatch on the pyroelectric properties of epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ thin films, *Phys. Rev. Lett.* **109**, 257602 (2012).

Presentations

1. J. C. Agar, R. V. K. Mangalam, A. R. Damodaran, G. Velarde, L. W. Martin, *Domain Wall and Intrinsic Contributions to Dielectric Permittivity in Epitaxial $PbZr_{1-x}Ti_xO_3$ Thin Films*, Materials Research Society Spring Meeting (Apr. 2014, San Francisco, CA).
2. L. W. Martin, *New Modalities for and Understanding of Strain Control of Properties in Ferroelectric Thin Films*, Materials Research Society Spring Meeting (Apr. 2014, San Francisco, CA). [Invited]
3. L. W. Martin, *The Science and Engineering of Functional Complex Oxide Thin Films*, Department of Physics Colloquium, Indiana University (Jan. 2014, Bloomington, IN). [Invited]
4. B. Bhatia, H. Cho, J. Karthik, J. Choi, D.G. Cahill, L.W. Martin, and W.P. King, "High Power Density Pyroelectric Energy Conversion using a MEMS Platform," MRS Fall Meeting, Boston, MA, 2013.
5. L. W. Martin, *Strain Version 2.0: Pushing the Edge of Epitaxial Strain Through Compositional Gradients*, Materials Research Society Fall Meeting (Dec. 2013, Boston, MA) [Invited]
6. B. Bhatia, H. Cho, J. Karthik, J. Choi, D.G. Cahill, L.W. Martin, and W.P. King, "Energy Conversion from $BaTiO_3$ Thin Films using the Pyroelectric Ericsson Cycle," ISHMT-ASME Heat and Mass Transfer Conference, IIT Kharagpur, India, 2013. (P K Sarma Award for Best Poster)
7. L. W. Martin, *Flexoelectric Effects in Compositionally Graded Ferroelectric Thin Films – Towards Strain 2.0*, IEEE International Symposium on Applications of Ferroelectrics Meeting (July 2013, Prague, Czech Republic) [Invited]
8. L. W. Martin, *Probing and Controlling Thermal-Electrical Responses in Exotic Ferroelectric Thin Films*, Department of Physics Colloquium, West Virginia University (April 2013, Morgantown, WV) [Invited]
9. L. W. Martin, *Fundamentals of Complex Oxide Thin-Film Growth and Characterization*, Invited Tutorial, American Physical Society March Meeting 2013 (March 2013, Baltimore, MD) [Invited]
10. L. W. Martin, *Domain Structures and Switching in Ferroelectric Thin Films*, 12th International Workshop on Piezoresponse Force Microscopy and Nanoscale Electromechanics: Theory, Techniques, and Applications, Oak Ridge National Laboratory (March 2013, Oak Ridge, TN) [Invited]
11. L. W. Martin, *"Mining" Existing Materials for Useful Functionalities – A Material Maker's Perspective*, National Science Foundation, Materials By Design II Workshop (Feb. 2013, Arlington, VA) [Invited]

12. L. W. Martin, *The Science and Engineering of Thermal-Electrical Responses of Materials*, Department of Materials Science and Engineering Colloquium, University of California, Berkeley (Feb. 2013, Berkeley, CA) [Invited]
13. J. Kardel, Z. Connell, J. Agar, J. Karthik, A. R. Damodarn, L. W. Martin, *Pyroelectric Properties of Epitaxial Ferroelectric Thin Films*, Fundamental Physics of Ferroelectrics and Related Materials 2013 (Jan. 2013, Ames, IA)
14. B. Bhatia, J. Karthik, T. Trong, D. G. Cahill, L. W. Martin, W. P. King, *Pyroelectric Measurements on $PbZr_{0.2}Ti_{0.8}O_3$ Epitaxial Layers*, Materials Research Society, Fall 2012 Meeting, Symposium AA: Oxide Nanoelectronics and Multifunctional Dielectrics (AA19.03) (Nov. 2012, Boston, MA)
15. J. C. Agar, J. Karthik, A. R. Damodaran, V. Mangalam, L. W. Martin, *Dielectric and Electrocaloric Properties of $PbZr_xTi_{1-x}O_3$ Thin Films Near the Morphotrophic Phase Boundary*, Materials Research Society, Fall 2012 Meeting, Symposium AA: Oxide Nanoelectronics and Multifunctional Dielectrics (AA9.31) (Nov. 2012, Boston, MA)
16. L. W. Martin, *Enhanced Thermal-Electrical Responses in Ferroelectric Thin Films*, Département de Physique de la Matière Condensée Colloquium, Université de Genève (March 2012, Geneva, Switzerland) [Invited]
17. L. W. Martin, *Engineering Thermal-Electrical Responses in Complex Oxides: Enhanced Dielectric and Pyroelectric Response in Epitaxially Strained Ferroelectric Thin Films*, Department of Materials Science and Engineering Colloquium, University of Michigan (Jan. 2012, Ann Arbor, MI) [Invited]
18. L. W. Martin, *Engineering Thermal Properties and Response of Epitaxial Oxide Thin Films for Advanced Devices*, Workshop on Oxide Electronics (Sept. 2011, Napa, CA) [Invited]
19. L. W. Martin, *Understanding and Manipulating Defects in Complex Oxide Materials – Implications for Properties and Devices*, HP Labs Colloquium (Sept. 2011, Palo Alto, CA) [Invited]
20. L. W. Martin, *Engineering Thermal-Electrical Responses in Complex Oxides: Enhanced Dielectric and Pyroelectric Response in Epitaxially Strained Ferroelectric Thin Films*, Department of Materials Science and Engineering Colloquium, University of California, Berkeley (Sept. 2011, Berkeley, CA) [Invited]

Solid State Cooling with Advanced Oxide Materials

Lane W. Martin, David G. Cahill, and William P. King

AFOSR Thermal Science Program Review

May 9, 2014

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Department of Mechanical Science and Engineering
Department of Electrical and Computer Engineering

Program Overview

Program overview and goals:

- Probe *electrocaloric* materials for solid state cooling
- Address gaps in the understanding of how to control and exploit these effects for real engineering systems
- Develop theoretical/experimental approaches to study thermodynamic properties and effects in thin film systems
- Design, synthesize, and study complex oxide materials possessing the capacity for enhanced solid state cooling
- Probe the potential for new modalities of cooling → how does one produce large field-driven entropic changes?

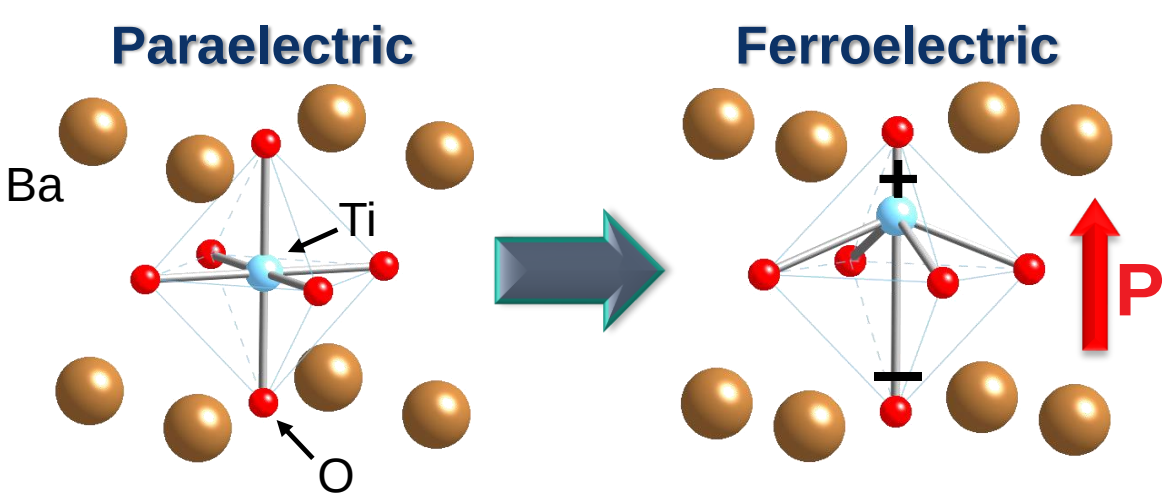
Program approach:

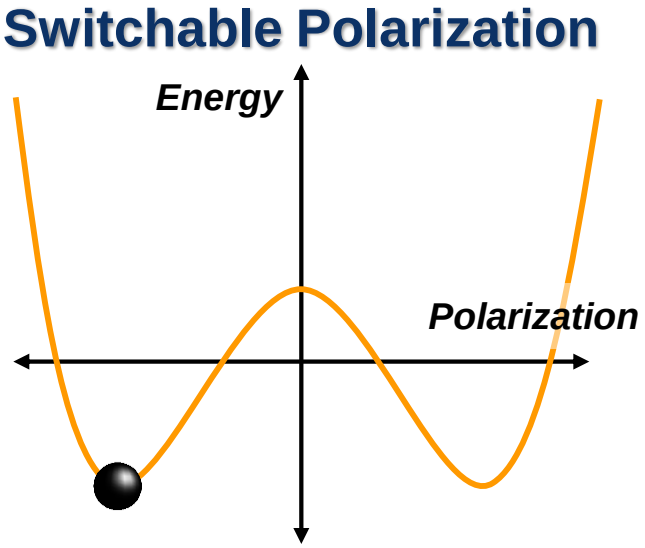
- Combined phenomenological modeling, advanced materials synthesis, and new measurement techniques to understand the fundamental materials science and engineering of solid state cooling materials

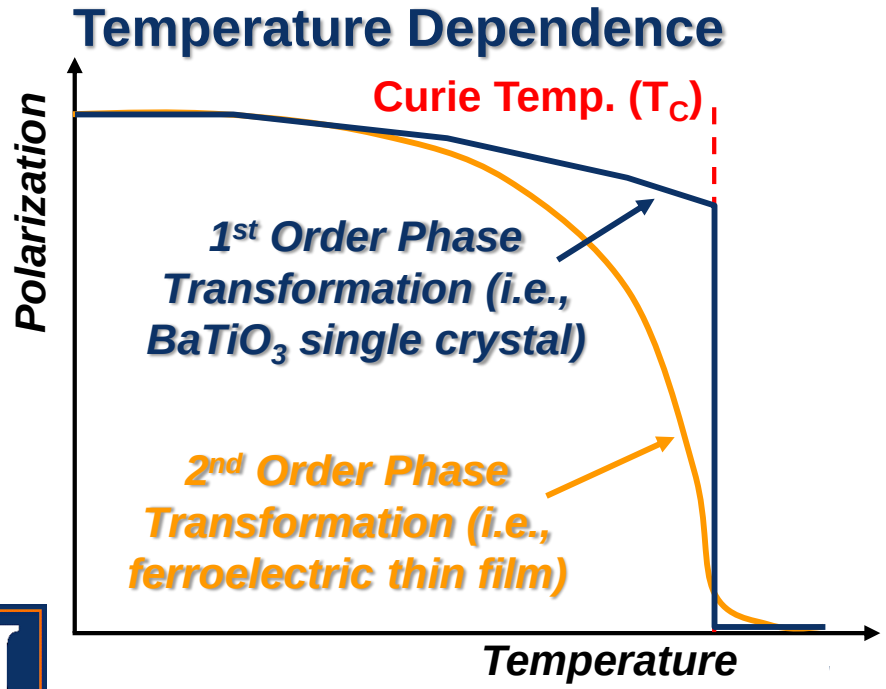
Program history and details:

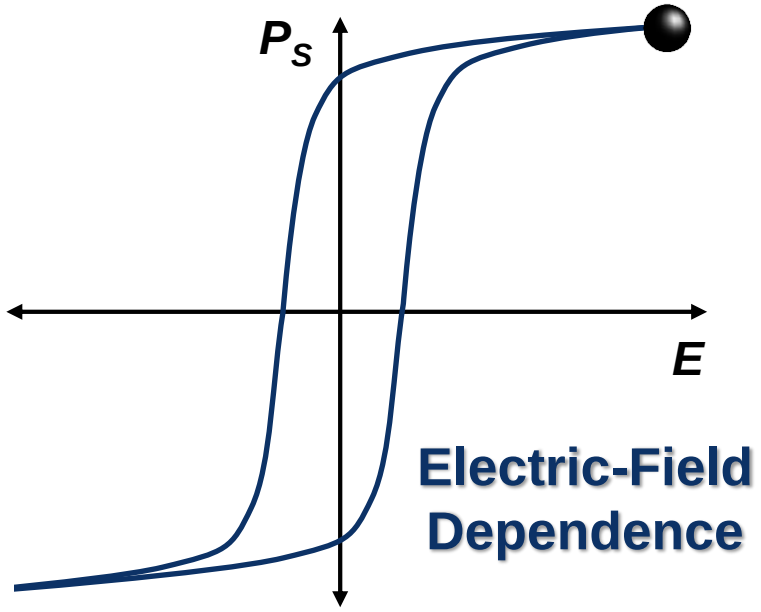
- Supported 2 graduate student researchers (spread across the three PIs)
- Program Managers: Dr. Kumar Jata, Dr. Joan Fuller, and Dr. Ali Sayir
- Funding Period: June 1, 2011 to May 31, 2014

Crash Course on Ferroelectrics (1)



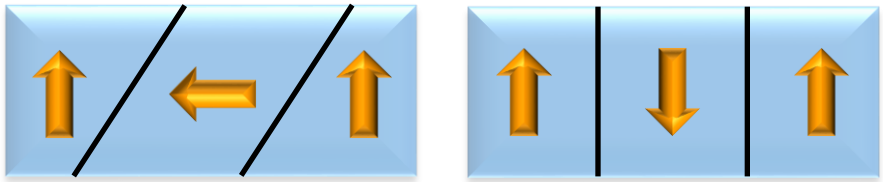






Crash Course on Ferroelectrics (2)

Domain walls in ferroelectrics



90° DW 180° DW

$$\chi_\alpha = \frac{d\langle P\rangle}{d\alpha} = \frac{d(\phi_c P_s)}{d\alpha}; \alpha = T, E, \sigma$$

$$= \phi_c \frac{dP_s}{d\alpha} + P_s \frac{d\phi_c}{d\alpha}$$

Intrinsic Extrinsic

Domain wall displacement → Extrinsic contribution to χ

Total Pyroelectric Coefficient (π)

$$\pi = \pi_i + \pi_e + \pi_s$$

Intrinsic π → ΔT gives rise to ΔP_s $\phi_c \left(\frac{dP_s}{dT}\right)$

Primary Pyroelectric Effect

Extrinsic π → Temp. dep. movement of domain walls $P_s \left(\frac{d\phi_c}{dT}\right)$

Secondary π → Diff. in thermal exp. between film/sub.

$$\propto d_{31}(\alpha_f - \alpha_s)$$

Zook and Liu, *J. Appl. Phys.* **49**, 4604 (1978)

Little work on role of these effects in thermal response

Electrocaloric Effect

- *Electrocaloric effect* (ECE) → adiabatic change of temperature that results from an electric field-driven change in polarization [$\Delta T \sim dS/dE$]
- Physical "reverse" of the pyroelectric effect (π) → temperature dependent change in polarization (dP/dT)

$$\pi = \left(\frac{dP}{dT}\right)_{\sigma,E} \leftrightarrow \Delta S = \int_{E_1}^{E_2} \left(\frac{dP}{dT}\right)_E dE \rightarrow \Delta T = -T \int_{E_1}^{E_2} \frac{1}{c_E}\left(\frac{dP}{dT}\right)_E dE$$

Maxwell relation

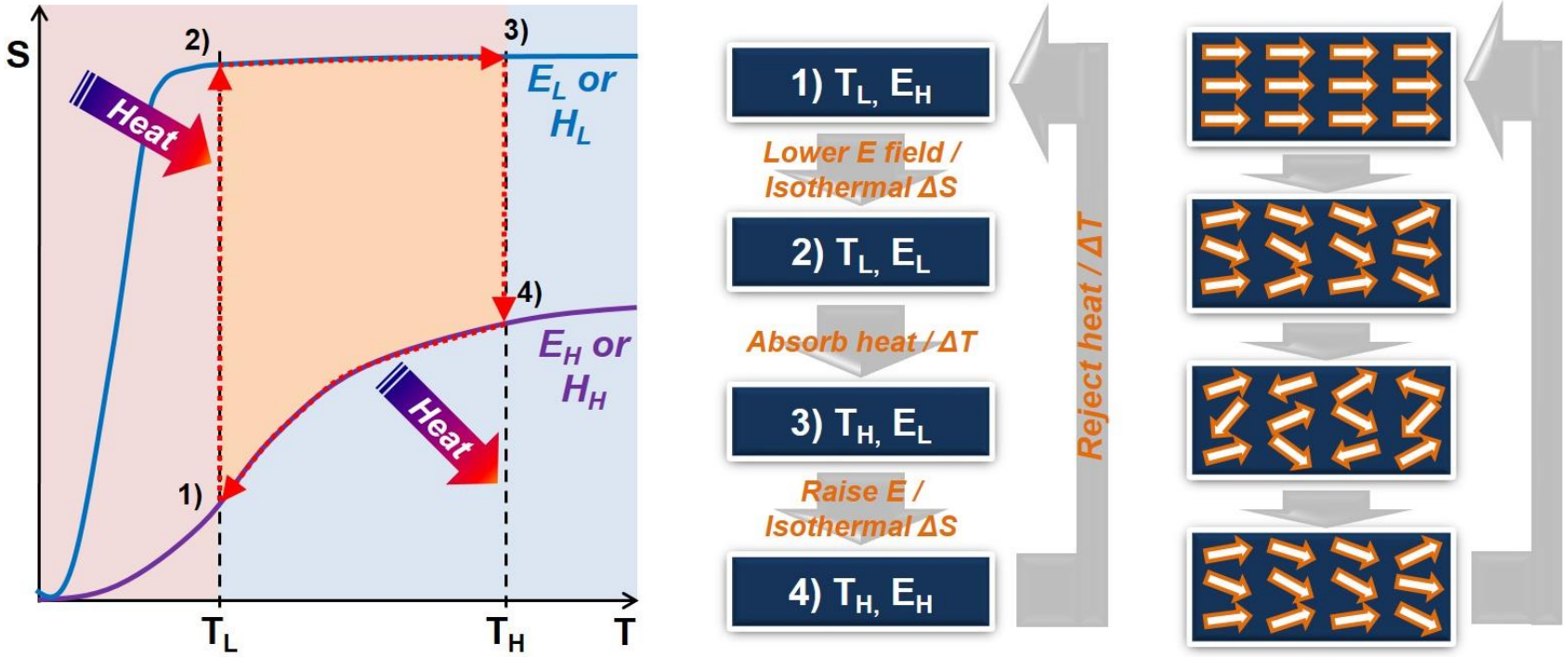
- Significant ECE requires…
  - A material with a large P and π → ferroelectric materials
  - Large entropy change associated with the polarization change → potentially operate ferroelectrics near or above T_C
  - Other sources of entropy → example from magnetocalorics

Large MCE in $Gd_5Ge_2Si_2$ → ***H***-induced structural change (entropy of spins and lattice)

Levin *et al. Phys. Rev. B* **62**, R14625 (2000); Choe *et al*. *Phys. Rev. Lett.* **84**, 4617 (2000); Morellon *et al*. *Phys. Rev. B* **58**, R14721 (1998); Meyers *et al*. *Phys. Rev. B* **66**, 012106 (2002)

Refrigeration Cycles

- The efficiency, cooling capacity of ECE can be improved using refrigeration cycles that utilize the intrinsic nature of the ferroic-cooling media
- Mimic gas-phase thermodynamic cycles such as Stirling or Ericsson cycles
- Ideal refrigeration cycle → Ericsson cycle consisting of two isotherms and two constant field (either electric or magnetic) processes



Lang, *Ferroelectrics* **11**, 519 (1976); Radebaugh *et al*., *Cryogenics* **19**, 187 (1979); Olsen *et al*., *J. Appl. Phys.* **58**, 4709 (1985); He *et al.*, *Inter. J. Therm. Sci.* **42**, 169 (2003).

Challenges and Opportunities

Despite considerable interest, a number of factors have limited the development of ECE materials for practical applications…

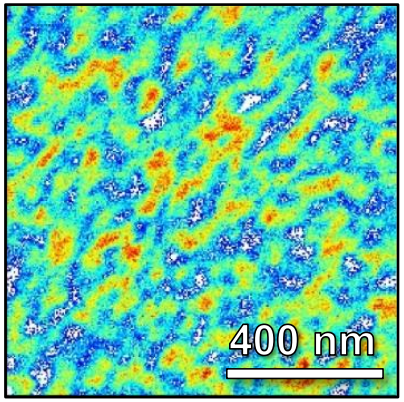
- Limited pathways to tune properties in these materials → need to identify new ways of enhancing performance of ECE materials (limiting losses)
- Imprecise testing methods → ΔS and ΔT are deduced from indirect measurements
    - Fundamental questions over the validity of these approaches
- Limits to the magnitude of $\boldsymbol{E}$ and $\boldsymbol{H}$ fields that can be applied to bulk samples

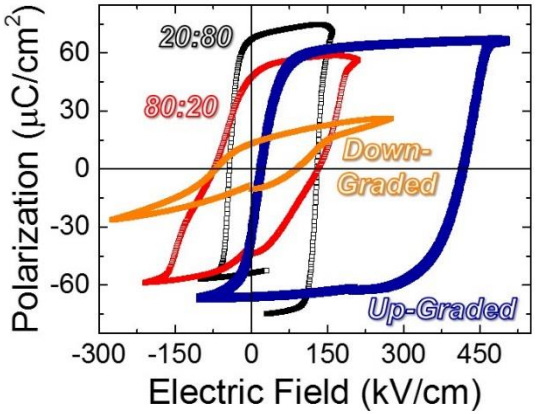
Our work aims to overcome these challenges…

- Comprehensive approach to the design, synthesis, and characterization of thin film oxides (something called for by researchers in the field)
- Assessing (un)common losses and limiting effects in these materials
- Explore new materials and routes to enhance field-induce entropic effects
- Develop methodologies to directly probe and distill the fundamental response of these materials in operation

Program Highlights

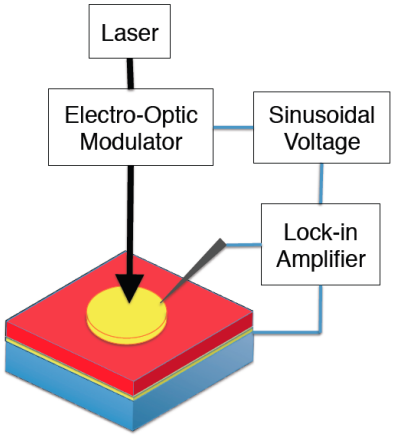
New Materials

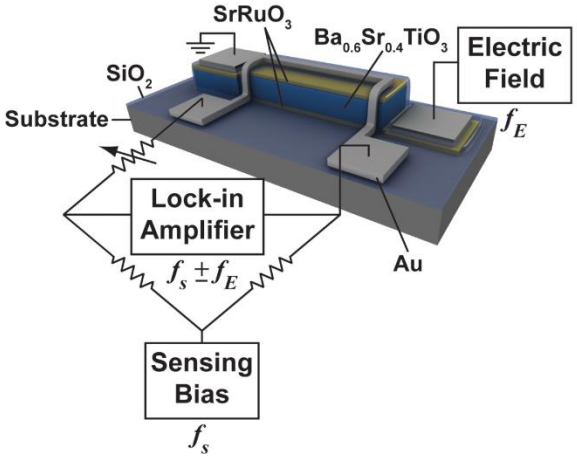




New materials with unprecedented property combinations

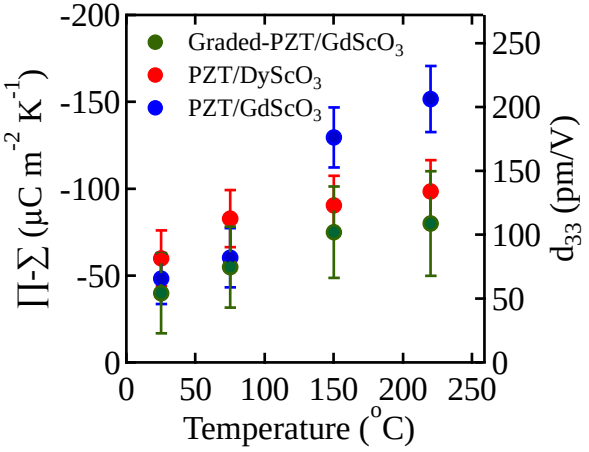
New Measurements

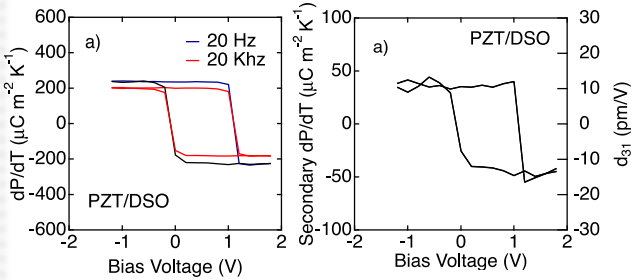




Pump-probe & nano-fabrication approaches to probe *T, S,…*

New Understanding

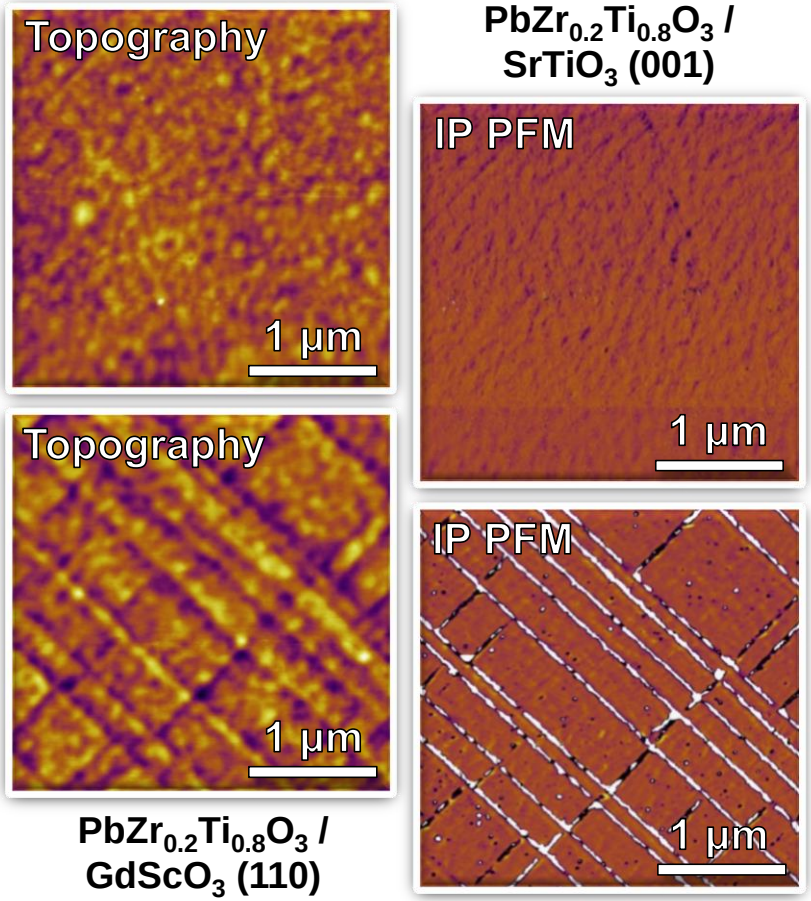




Domain wall & elasto-caloric effects, failures in measurements

Domain Contributions to Thermal Response

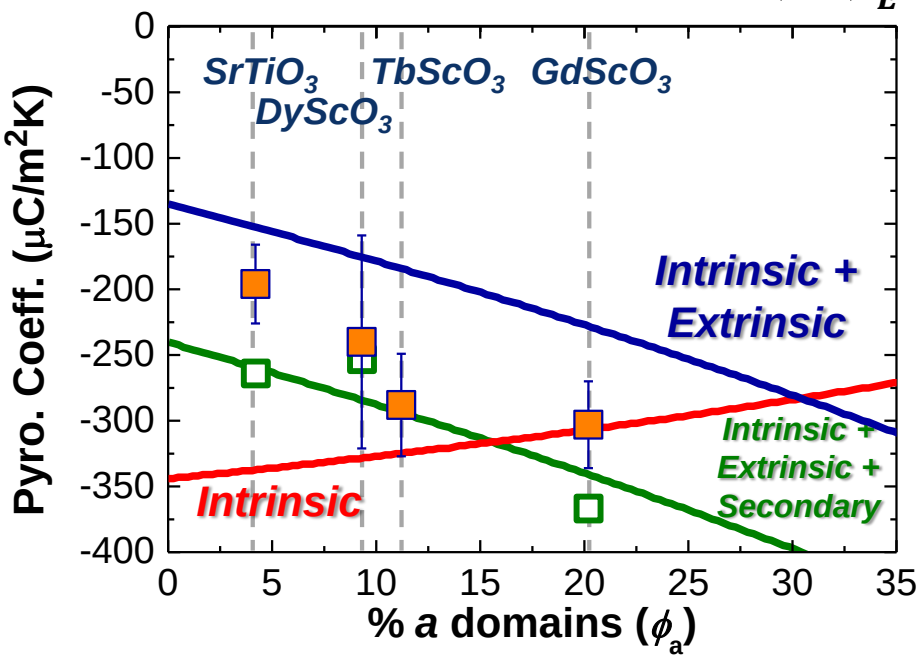
Use our control of materials to advance our understanding of thermal response…



- Epitaxial strain → control domain structures/densities

Karthik, *et al.*, *Phys. Rev. Lett.* **108**, 167601 (2012)

Pyroelectric coefficient $\pi = \left(\frac{dP}{dT}\right)_E$

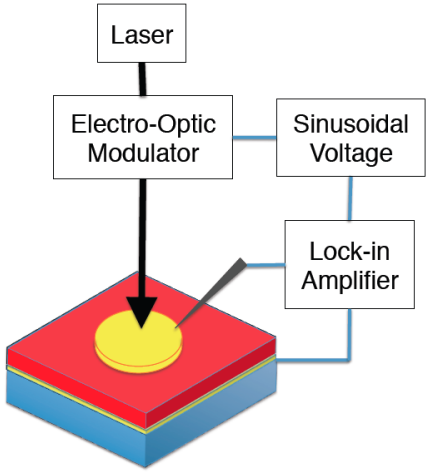


- π is strongly effected by extrinsic (domain wall) contribution
- Thermal expansion mismatch (secondary effect) between film and substrate → key to understanding performance

New Probes of Thermal Response in Films

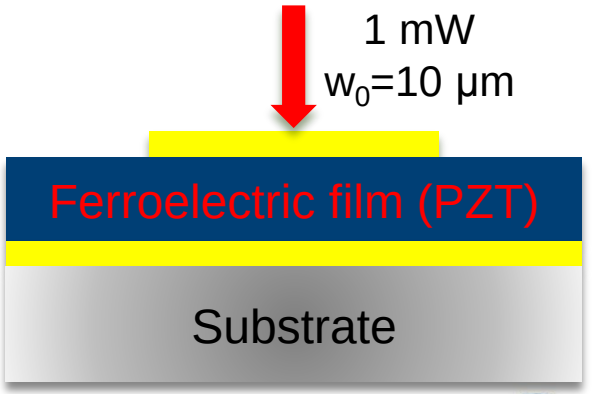
Wide-Frequency Optical Probes of Thermal Response

- Laser-based approaches → distinguish various contributions to response
- Leverage the high-quality epitaxial capacitors
- Measurements of the thermal properties by TDTR
  - Multilayer thermal diffusion model, cylindrical coordinates



$$I(f) = 2\pi \frac{dP(f)}{dT} \int_0^h \int_0^a \frac{dT(f,r,z)}{dt} r dr dz$$

- Measure current from 1 Hz to 10 MHz
  - Current preamp for f < 1 kHz
  - 50 ohm load and voltage preamp for f > 1 kHz
  - Programmable low-pass filter for f > 100 kHz and rf lock-in

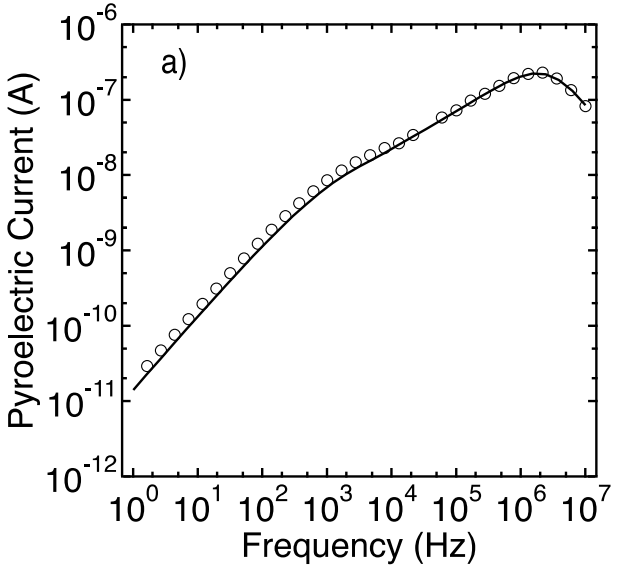


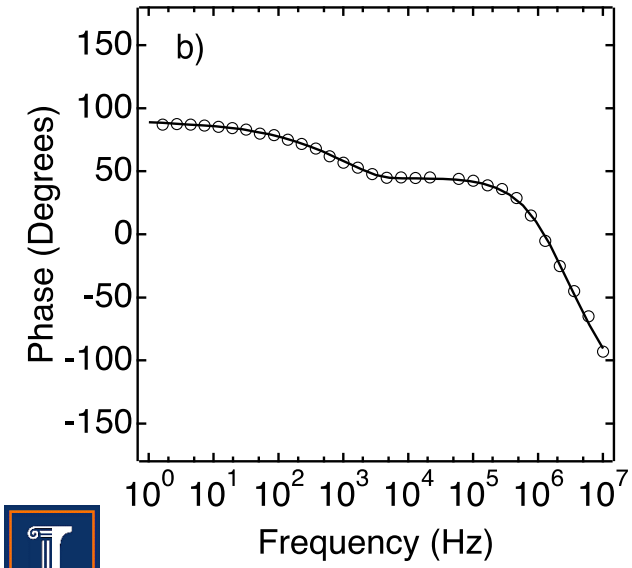
Steady-state ΔT≈5 K

$r = a = 50$ μm
$z = h = 150$ nm

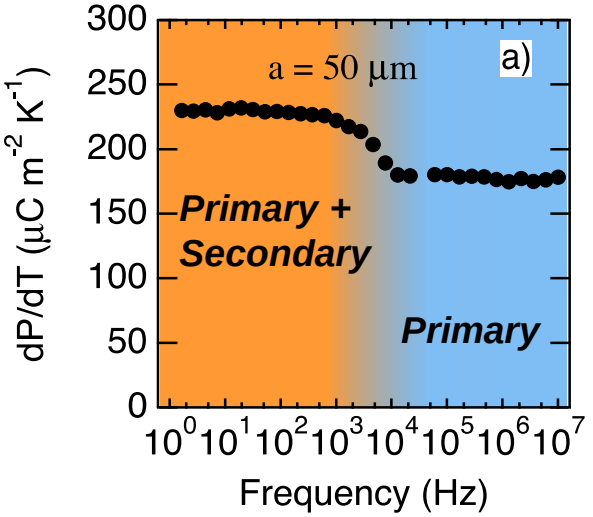
T. Trong, *et al.*, in preparation May 2014

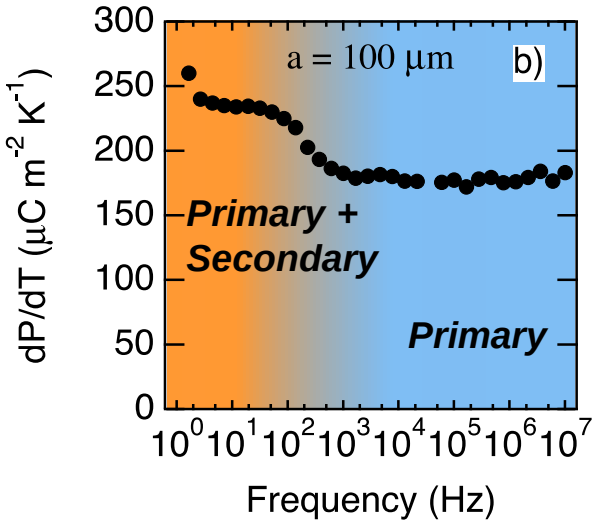
f-dependent Probes of Thermal Response





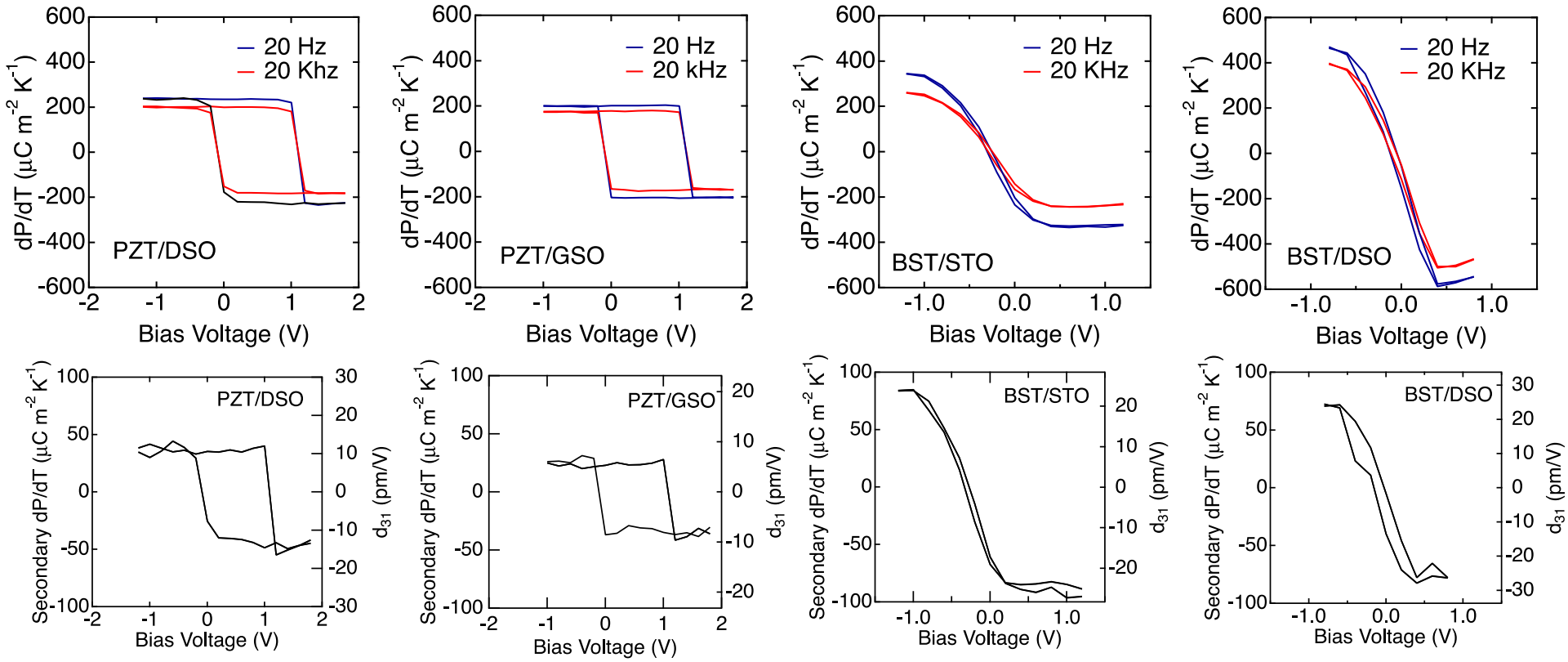
- Laser-based methods provide the ability to probe pyroelectric responses across unprecedented f-ranges
- Slope of the response of the material is found to change with f – why?
- f-dependent change varies with capacitor size
- Change f can change thermal penetration depth – probe effects only in film and from film/substrate combo
- ***Separate Primary and Secondary contributions***





T. Trong, *et al.*, in preparation May 2014

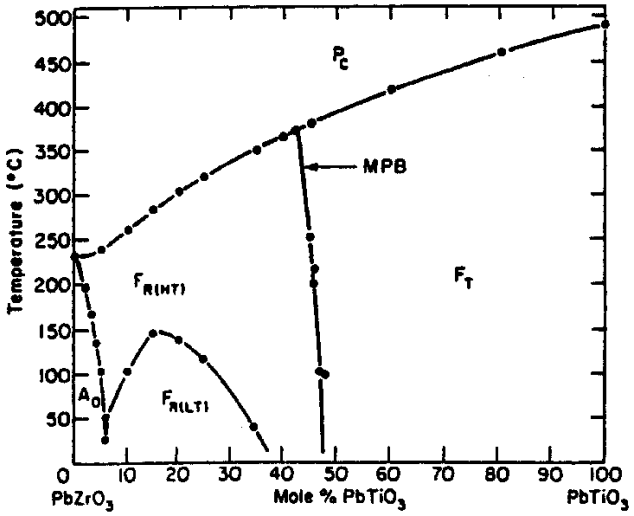
Separating Primary and Secondary Effects

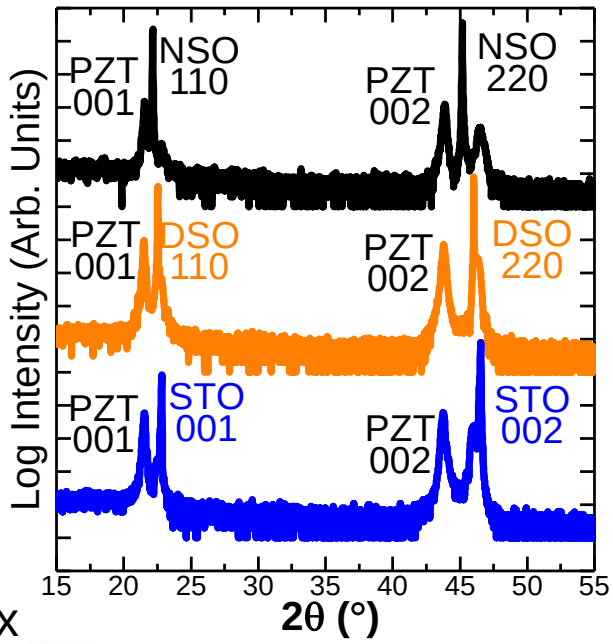


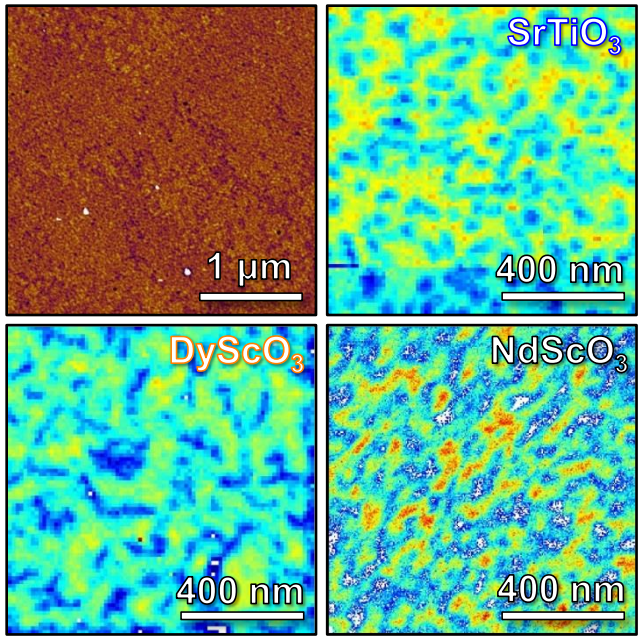
- **This method enables us to deterministically separate *primary* and *secondary* contributions to thermal response in materials**
- **Identification of systems where secondary effects are large**
- **Implications for performance of thin-film devices at high frequency**

T. Trong, *et al.*, in preparation May 2014

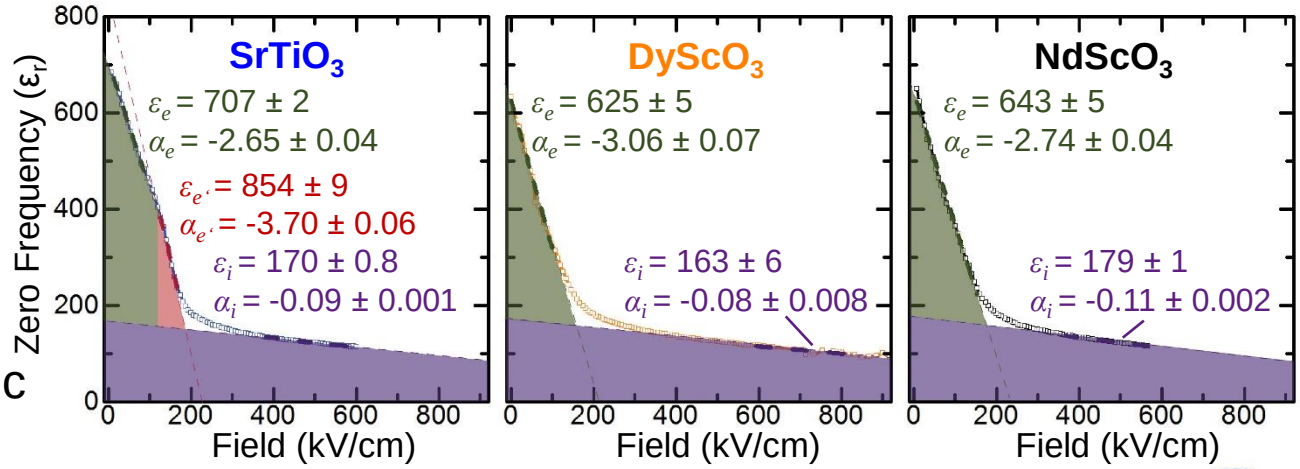
New Materials – $PbZr_{0.52}Ti_{0.48}O_3$





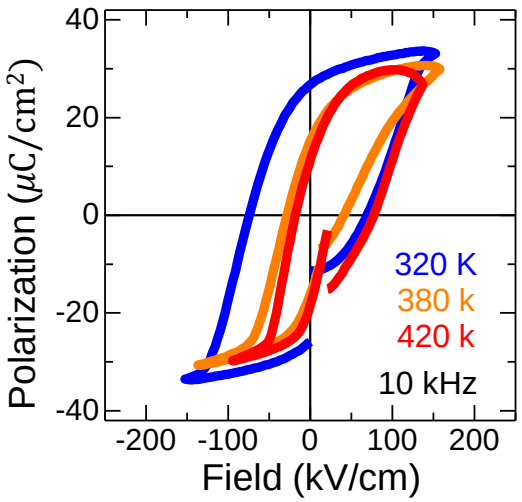


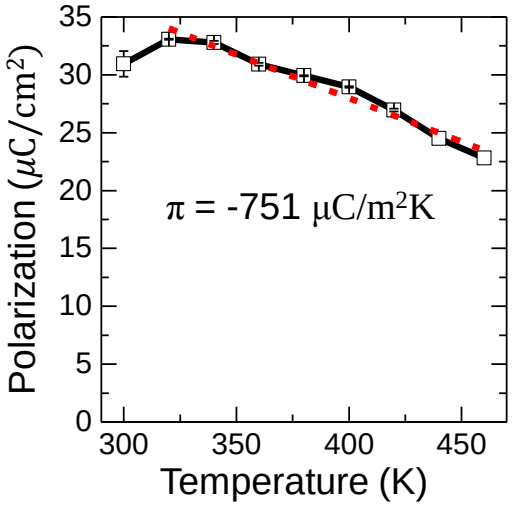
- Morphotropic phase boundary (MPB) → complex structural competition
- Arguably "best" MPB films ever produced
- First imaging of domain structure
- Complex strain evolution impacts properties (intrinsic vs. extrinsic effects)

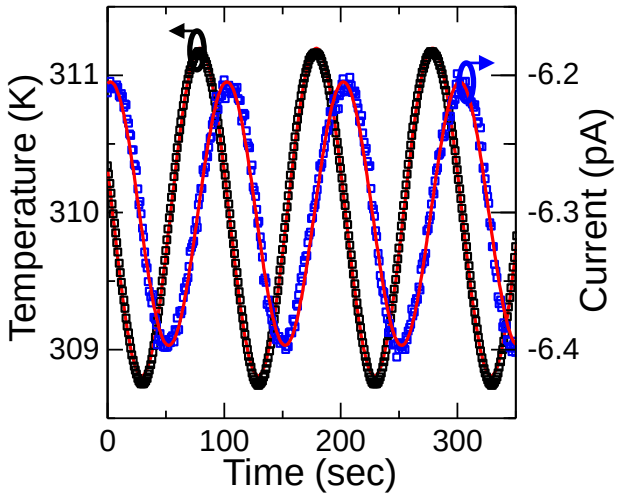


J. C. Agar, *et al.*, accepted *Adv. Mater. Interfaces* (April 2014)

New Materials – $PbZr_{0.52}Ti_{0.48}O_3$





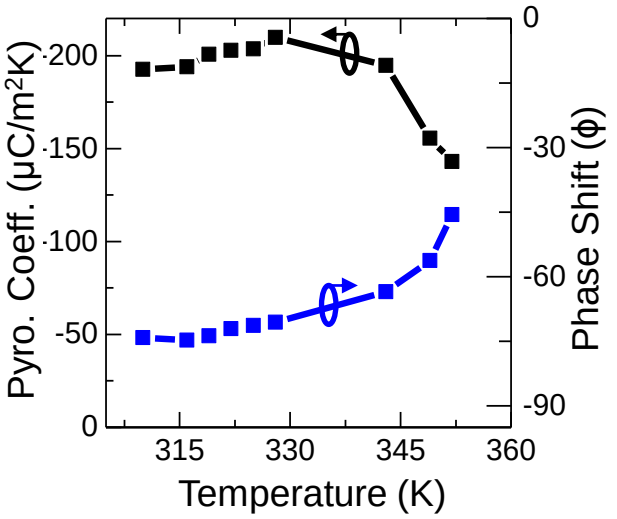


- Initial probes of thermal response underway
- Comparison of direct and indirect measurements
- **Indirect** → Probe ΔP/ΔT and calculate pyroelectric coefficient (π) assuming T-independent over given ΔT
- **Direct** → Probe pyroelectric current (i_p)

$$T = T_b + T_0 sin(\omega t)$$

$$i = i_0 sin(\omega t + \phi)$$

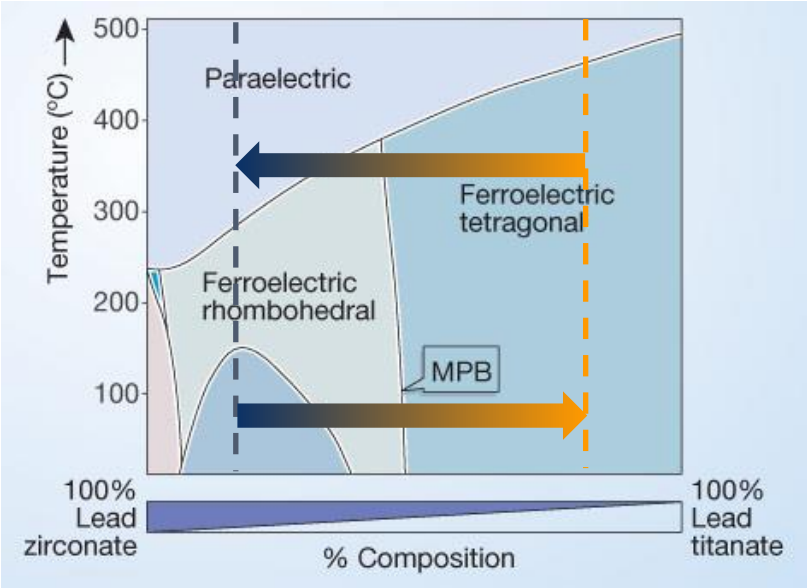
$$\pi = \frac{i_0 \sin(\phi)}{A T_0 \omega}$$



Traditional methods have their limitations → must be careful to probe the real effects…motivation for development of novel methods

New Materials – Compositionally-Graded

$PbZr_{1-x}Ti_xO_3$ Phase Diagram



E.Cross, *Nature* **432**, 24 (2004)

- 100 nm thick $PbZr_xTi_{1-x}O_3$
- $PbZr_{0.8}Ti_{0.2}O_3$ (a = 4.118 Å and α = 89.73º)
- $PbZr_{0.2}Ti_{0.8}O_3$ (a = 3.94 Å and c = 4.12 Å)
- $GdScO_3$ substrate (a = 3.97 Å)

Heterostructures

PZT 80:20

$PbZr_{0.8}Ti_{0.2}O_3$

Substrate

3.5% compressive

PZT 20:80

$PbZr_{0.2}Ti_{0.8}O_3$

Substrate

0.8% tensile

Down-Graded

$PbZr_{0.2}Ti_{0.8}O_3$

$PbZr_{0.8}Ti_{0.2}O_3$

Substrate

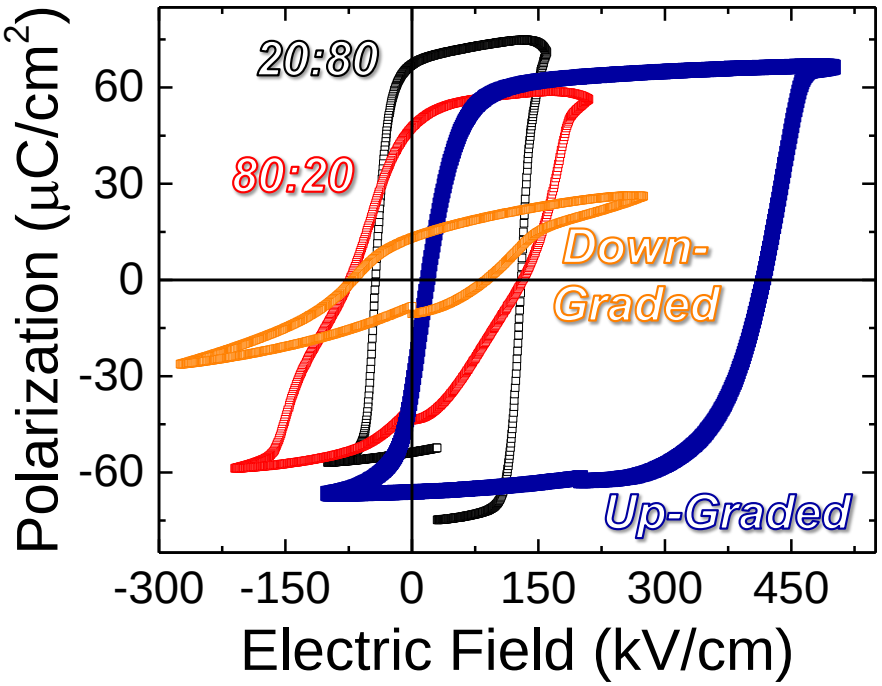
Up-Graded

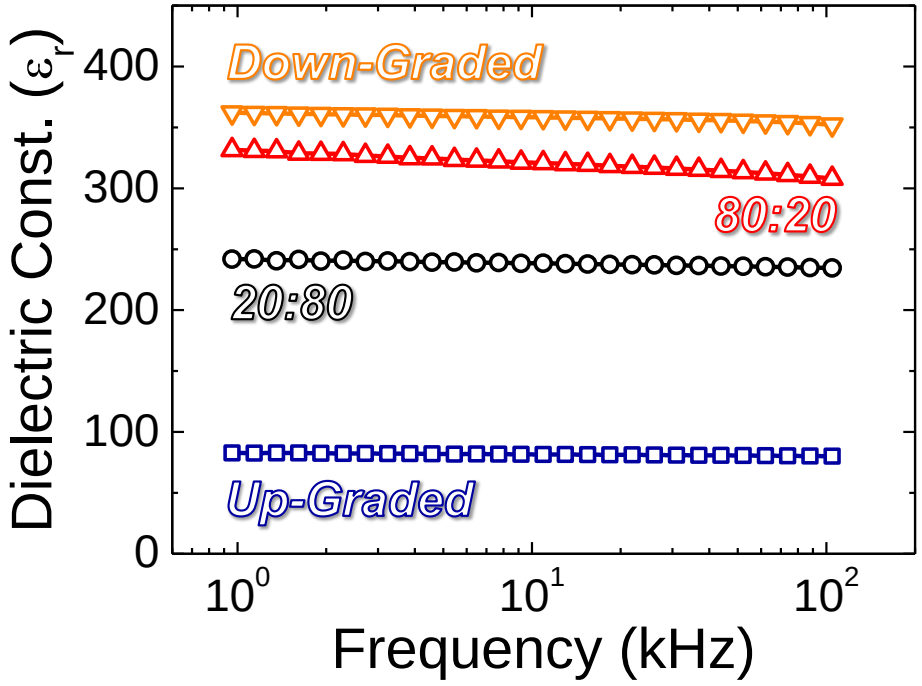
$PbZr_{0.8}Ti_{0.2}O_3$

$PbZr_{0.2}Ti_{0.8}O_3$

Substrate

Ferroelectric & Dielectric Properties





- **Down-Graded**
  - Reduced polarization → >1/2 of the film possess *in-plane* oriented domains which cannot be swtiched
  - High dielectric constant → large extrinsic contribution from domains
- **Up-Graded**
  - Large polarization, shifted loop → fully *out-of-plane* oriented domains, large built-in potential (flexoeletric effect)
  - Low dielectric constant → built-in field skews energy landscape

Mangalam, *et.al.*, *Adv. Mater.* **25**, 1761 (2013); *ACS Appl. Mater. Interfaces* **5**, 13235 (2013).

Additional theory development underway

Implications for Applications

Figure of merit for thermal applications (*i.e.*, energy conversion, solid state cooling, infrared sensing, and electron emission) are similar

$$FoM_{Image} = \frac{\pi}{C_P \varepsilon_r \varepsilon_0} \qquad FoM_{EC/Cool} = \frac{\pi^2 T}{C_P \varepsilon_r \varepsilon_0}$$

Heterostructure	π (μC/m²K)	ε_r (100 kHz)	C_P (J/cm³K)	FoM_{Image} (x10⁻², m²/C)	$FoM_{EC/Cool}$ (x10⁻³, 300K)
$PbZr_{0.2}Ti_{0.8}O_3$	-300 ± 7	235	~3	4.81	4.33
$PbZr_{0.8}Ti_{0.2}O_3$	-229 ± 11	453		1.90	1.31
Up-Graded	- 291 ± 4	85		12.9	11.3
Down-Graded	-185 ± 13	409		1.70	0.95
$LiNbO_3$	-83	31	2.8	10.8	2.69
$LiTaO_3$	-176	54	3.2	11.6	6.15

Mangalam, *et.al.*, *Adv. Mater.* **25**, 1761 (2013)
Mangalam, *et al.*, *ACS Appl. Mater. Inter.* **5**, 13235 (2013)

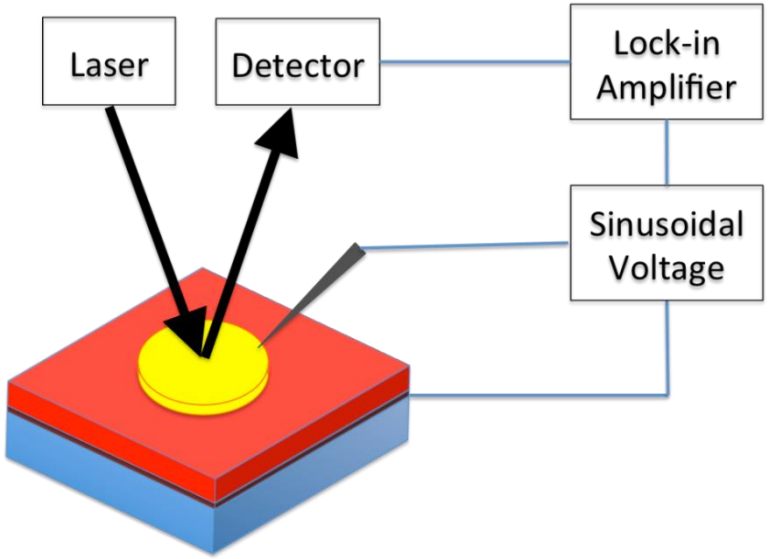
Up-graded heterostructures…

- **Improved FoMs → low dielectric permittivity → large pyroelectric coefficient**
- **Built-in electric field→ diminishes extrinsic contribution**

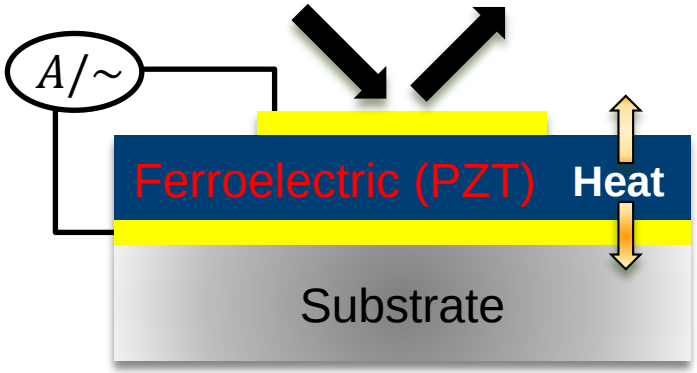
New Effects: dP/dT vs. dS/dE in Films

First Laser-based Probes of *dS/dE* in Epitaxial Layers

- Measure *dP/dT* through laser-driven ΔT current production
- Measure *dS/dE* through field-driven ΔT
  - ΔT probed by thermoreflectance (*dR/dT*) of top contact

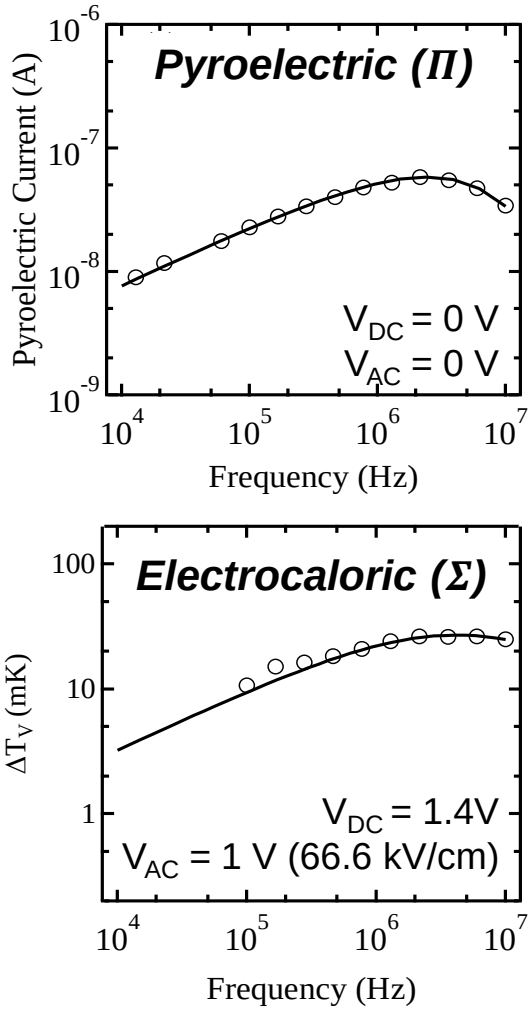


- Optimal frequency → thermal penetration depth in the PZT layer is on the order of the PZT thickness
- At high frequencies, 1D model of the thermal transport is sufficient
- Oscillating heat flux generated by the PZT layer diffuses in both directions

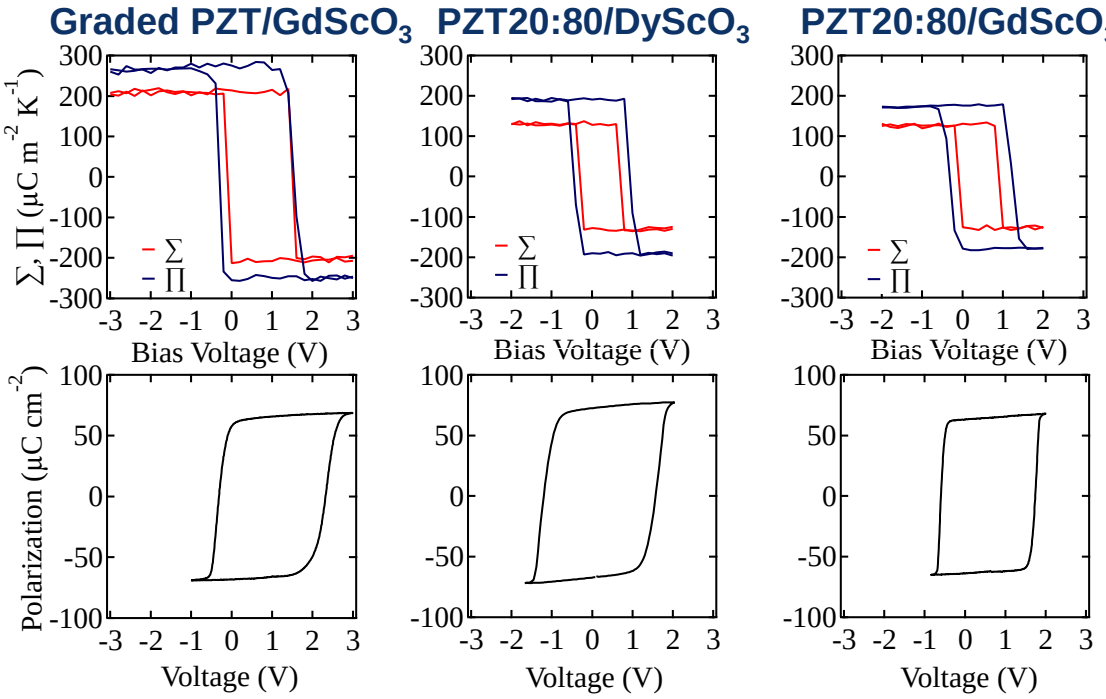


T. Trong, *et al.*, under review *Phys. Rev. Lett.* May 2014

Pyroelectric and Electrocaloric Loops



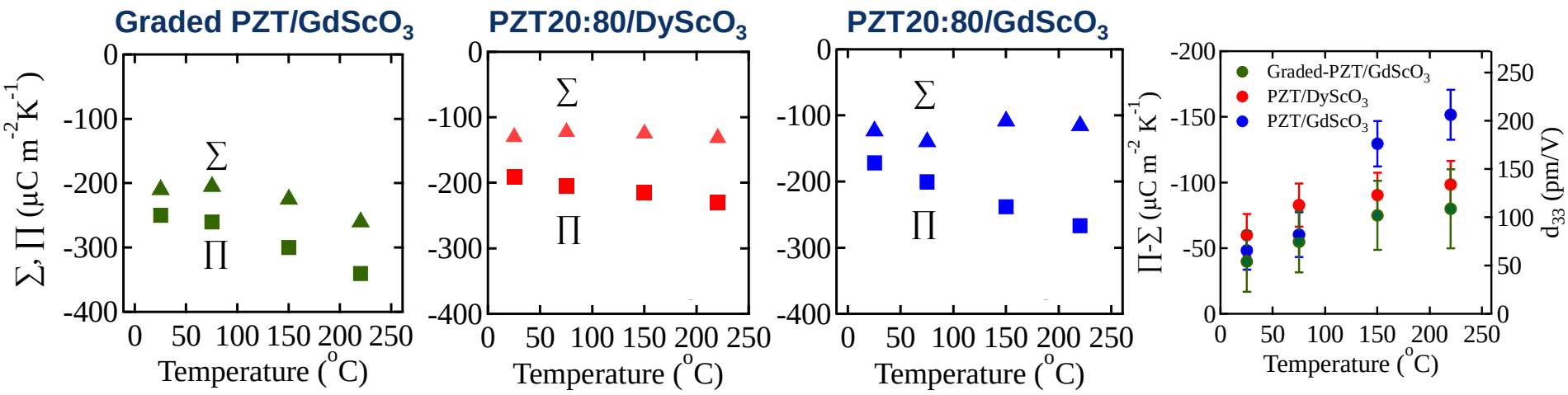
- Using laser-based approaches we can measure both pyroelectric (laser-induced current) or electrocaloric temperature change (field-induced ΔT) in thin films
- Direct comparison of Π and Σ → measurement at same field



- **New type of measurement (*ΔE* fixed, vary V_{DC}) → better picture of how adiabatic temperature change varies with polarization state**
- ***Π* and *Σ* are not equal → Maxwell relation fails…**

T. Trong, *et al.*, under review
Phys. Rev. Lett. May 2014

Limitations of Indirect Measurements of ΔT

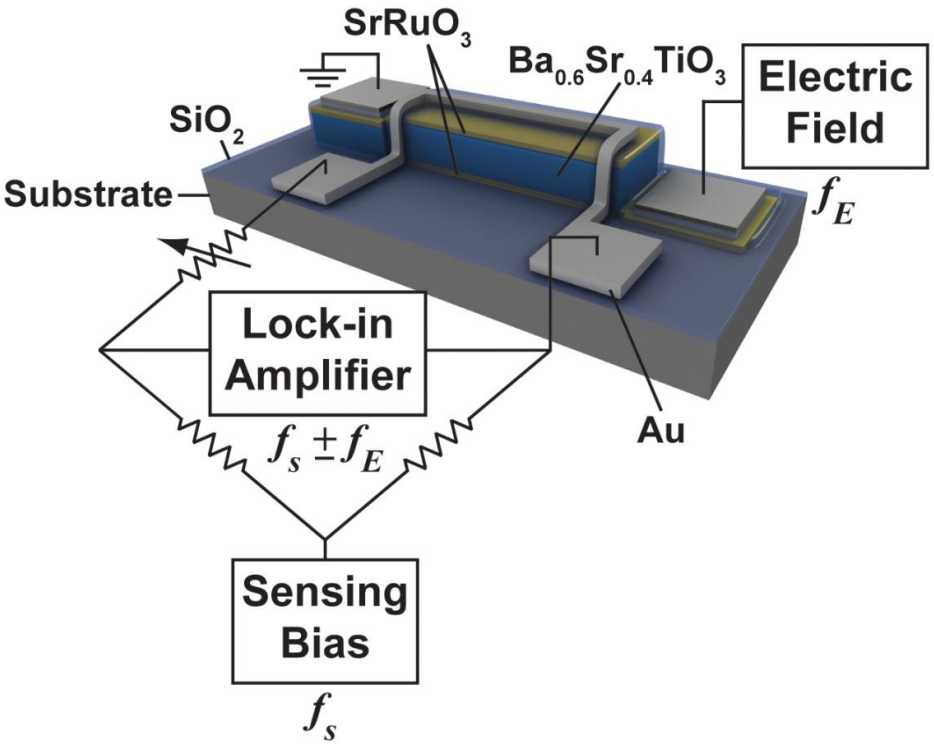


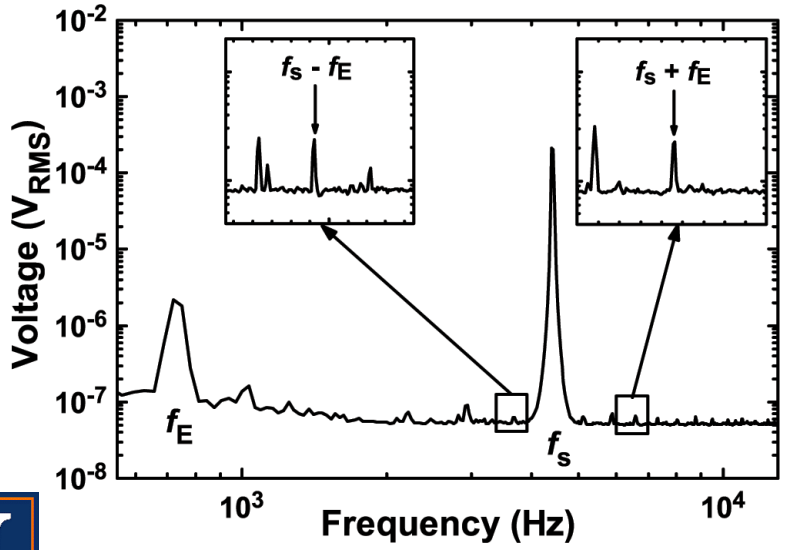
- **Hypothesis**: piezoelectric effect causes lattice expansion, lowers the frequencies of the lattice vibrations, increases the vibrational entropy → ***Elastocaloric effect***
- The elastocaloric effect *opposes* the electrocaloric effect (***Π > Σ***)
- Assume that the difference between the measured *dS/dE* and *dP/dT* is the change in vibrational entropy
- Solving for d_{33} yields physically reasonable values
  - **Indirect measurements of *ΔT* would miss these effects → overestimate electrocaloric effects**
  - **Control over competing electrocaloric/elastocaloric effects needed**

T. Trong, *et al.*, under review *Phys. Rev. Lett.* May 2014

Electrocaloric Devices/Measurements

- Realistic device structures have been probed
- Microfabricated platform allows independent ***E*** and ***T*** sensing
- An out-of-plane ***E*** is applied to the thin film at f_E
- Sensing current at f_s along the gold strip allows electrocaloric ***ΔT*** induced electrical resistance change measurement





- A bridge circuit is used to null out the sensing signal
- The electrocaloric temperature change signal is obtained at frequencies $f_s \pm f_E$ and can be measured using a lock-in amplifier

Thermal Modeling of Devices

- Induced electrocaloric ***ΔT*** is a function of the ***E*** frequency
- Model relates the applied out-of-plane ***E*** and thermometer sensing voltage with the output ***V*** measured by the lock-in amplifier at different frequencies
- Model includes competing contributions from electrocaloric cooling and Joule heating (which can be significant for low electrical resistance R_L films)

Input → Film out-of-plane voltage: $V_E = V_{DC} + V_{0E}\sin(\omega_E t)$

Sensing voltage: $V_s = V_{0s}\sin(\omega_s t)$

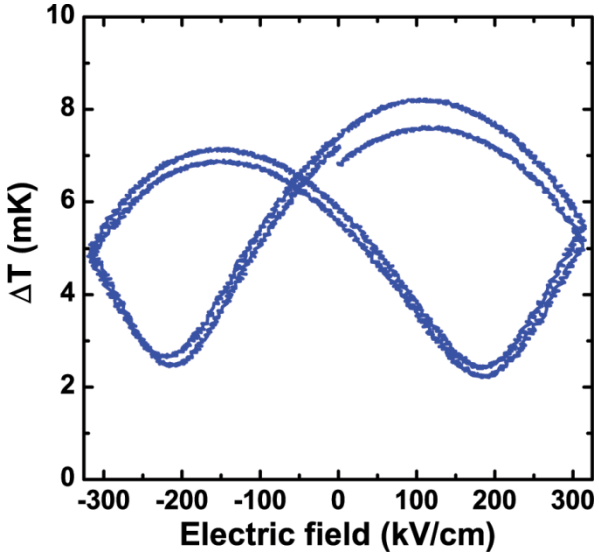
Output → $$V_{\omega_s \pm \omega_E} = \frac{1}{2}\frac{\alpha}{2\pi\Lambda_s l}\left(\underbrace{\frac{TpA\omega_E V_{0E}}{2\pi}}_{\text{Electrocaloric}} + \underbrace{\frac{2V_{DC}V_{0E}}{R_L}}_{\text{Joule Heating}}\right)V_{0s}\,Z_{LHOS}(\omega_E)$$

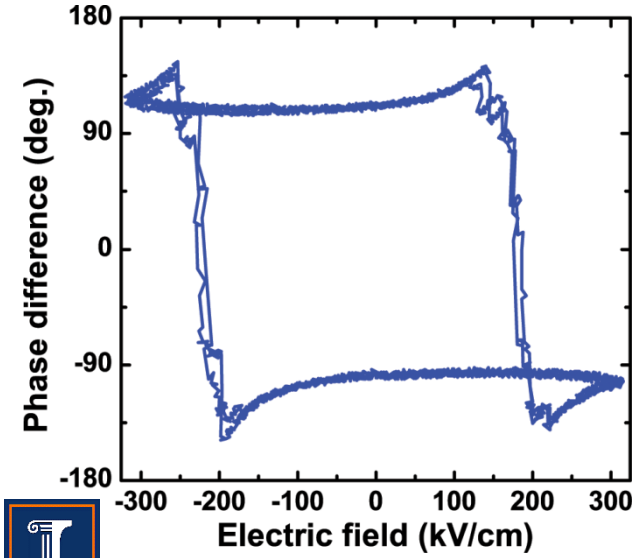
$$\Delta T = \frac{2V_{\omega_s \pm \omega_E}}{V_{0s}\alpha}$$

where $Z_{LHOS}(\omega_H) = \ln\omega_H + \ln\left(\frac{b^2}{D_{sub}}\right) + j\frac{\pi}{2}$ is the *Thermal Transfer Function*

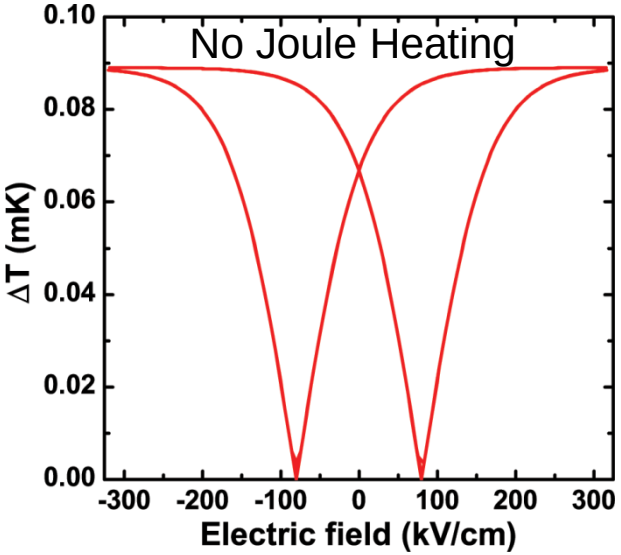
Electrocaloric Cooling – *E* Dependence

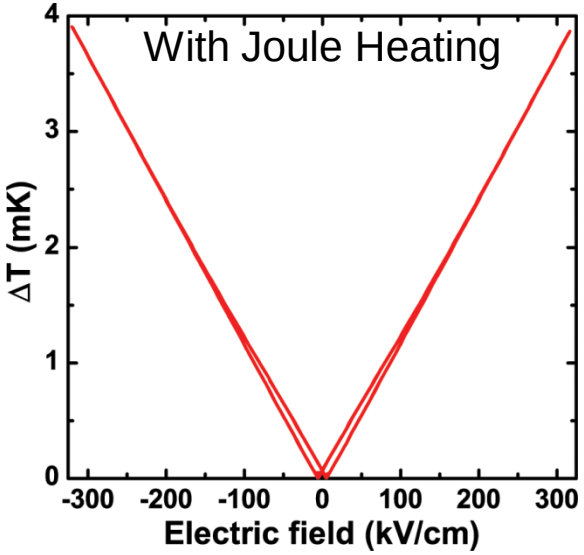
Measurement





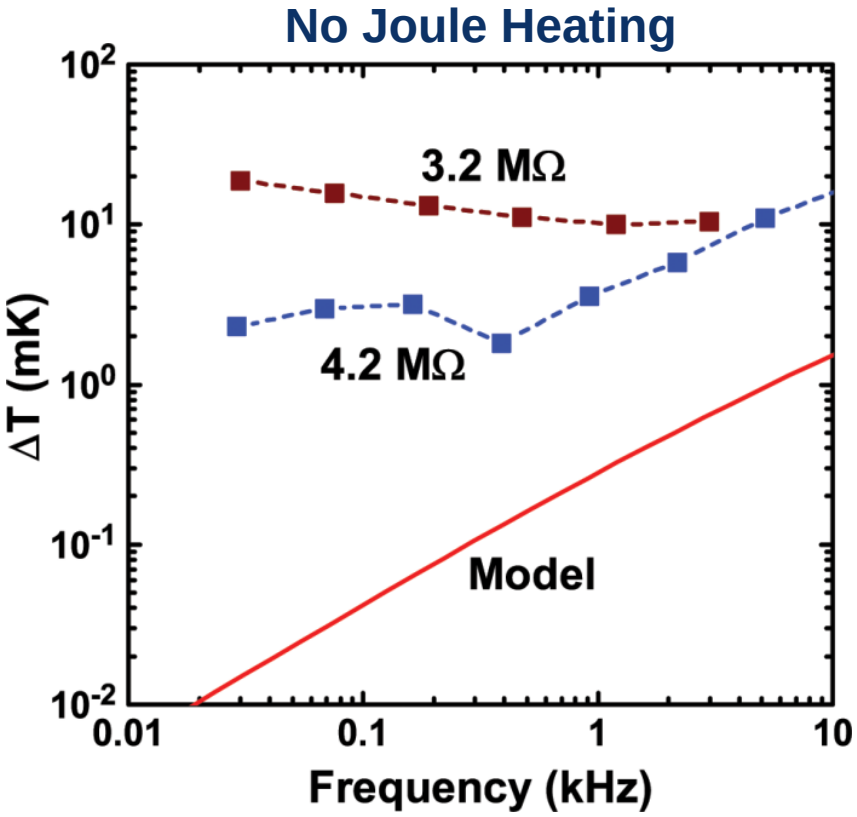
Model

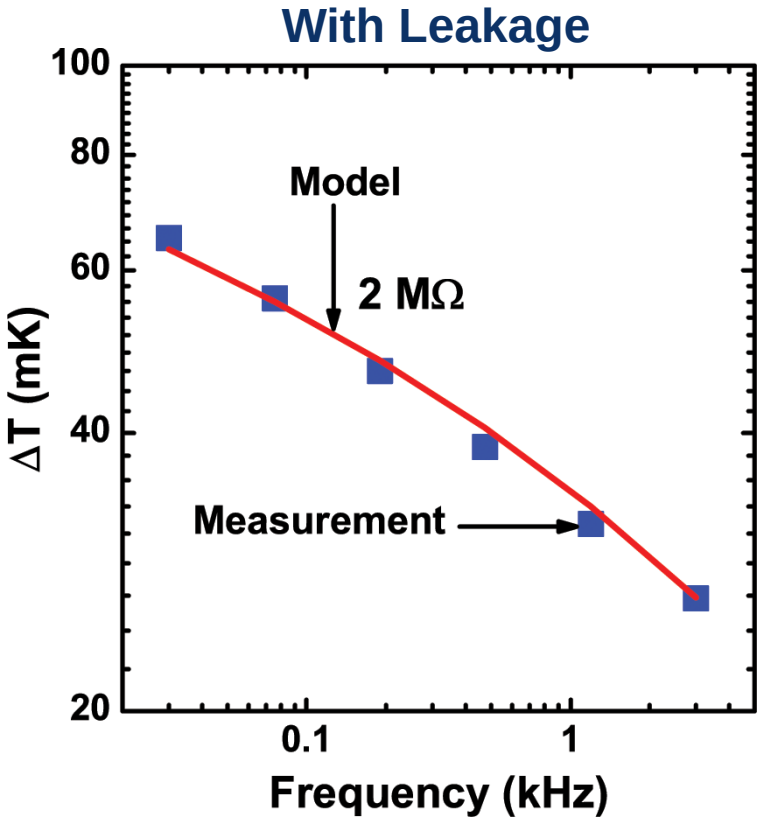




- ***A*** and ***ϕ*** difference of the ***T*** oscillation measured as a function of ***E*** → characteristic hysteretic behavior expected from electrocaloric **Δ*T***
- The measured **Δ*T*** amplitude → higher than predicted by electrocaloric **Δ*T*** alone
- Joule heating due to resistive leakage → explains the high amplitude of the measured **Δ*T***

Electrocaloric Cooling – Freq. Dependence

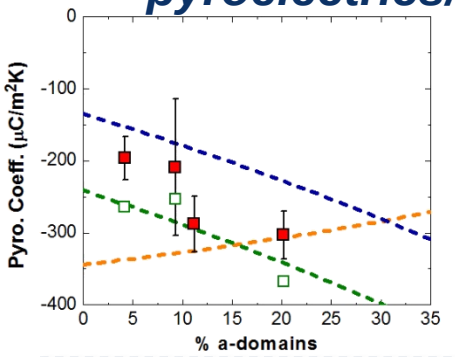




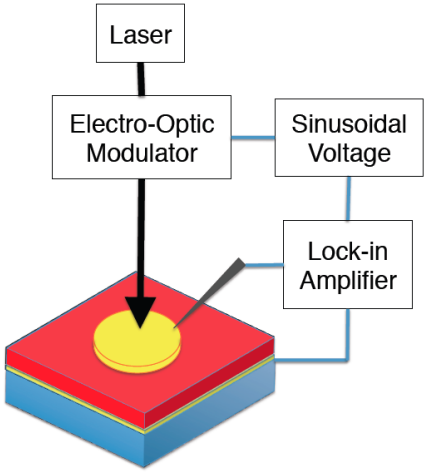
- Frequency-dependence of measured/modeled Δ*T* for different thin film devices with varying electrical resistance.
- Match between the frequency-dependence of the measured/modeled Δ*T* is obtained for films with high resistance → must work to limit losses

Summary of Results and Findings

Quantification of intrinsic, extrinsic, secondary, and elastocaloric effects in pyroelectrics/electrocalorics



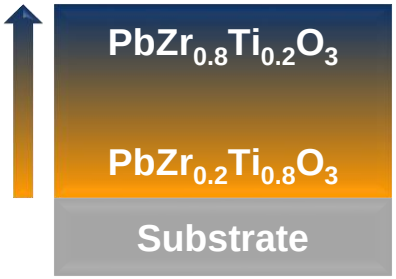
Domains walls, thermal mismatch, coupling between lattice and polarization are key



New measurements that overcome challenges in existing methods

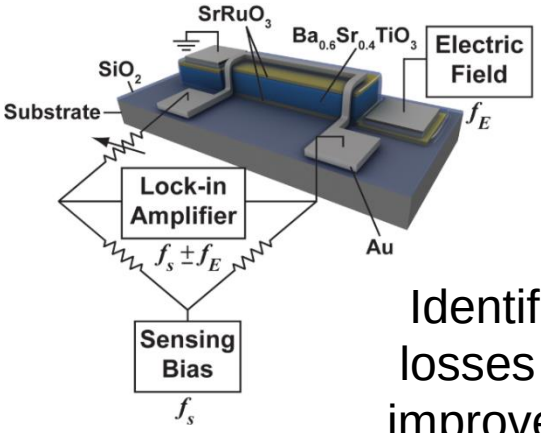
Access to wide *f*, *I*, and *T* ranges and routes to exclude spurious effects

Up-Graded



Development, testing, and demonstration of new high-performance materials for pyroelectric/electro-caloric applications

Enhanced figures-of-merit are possible



Demonstration devices and realistic operation probed

Identification of key losses and routes to improve performance

Publications: 5 accepted, 3 under review, 2 in preparation
Presentations: 14 invited, 6 contributed student (1 best poster award)

Program Accomplishments: Publications

1. T. Tong, J. Karthik, L. W. Martin, D. G. Cahill, Secondary effects in wide frequency range measurements of the pyroelectric coefficient of $Ba_{0.6}Sr_{0.4}TiO_3$ and $PbZr_{0.2}Ti_{0.8}O_3$ epitaxial layers, in preparation May 2014.
2. R. Xu, J. Zhang, Z.-H. Chen, J. Karthik, L. W. Martin, Orientation dependent structural phase diagrams and dielectric properties of $PbZr_{1-x}Ti_xO_3$ Part I. monodomain thin films, under review at *Phys. Rev. B* May 2014.
3. J. Z. Zhang, R. Xu, A. R. Damodaran, Z.-H. Chen, L. W. Martin, Understanding order in compositionally-graded ferroelectrics: flexoelectricity, gradient, and depolarization field effects, accepted *Phys. Rev. B* May 2014.
4. T. Tong, J. Karthik, R. V. K. Mangalam, L. W. Martin, D. G. Cahill, Reduction of the electrocaloric entropy change of ferroelectric $PbZr_{1-x}Ti_xO_3$ epitaxial layers due to an elastocaloric effect, under review at *Phys. Rev. Lett.* May 2014.
5. J. C. Agar, R. V. K. Mangalam, A. R. Damodaran, G. Velarde, J. Karthik, M. B. Okatan, Z. H. Chen, S. Jesse, N. Balke, S. V. Kalinin, L. W. Martin, Tuning susceptibility via misfit strain in relaxed morphotropic phase boundary $PbZr_{1-x}Ti_xO_3$ epitaxial thin films, accepted *Adv. Mater. Interfaces* (2014). (DOI: 10.1002/admi.201400098)
6. R. V. K. Mangalam, J. C. Agar, A. R. Damodaran, J. Karthik, L. W. Martin, Improved pyroelectric figures of merit in compositionally graded $PbZr_{1-x}Ti_xO_3$ thin films, *ACS Appl. Mater. Interfaces* **5**, 13235 (2013).
7. R. V. K. Mangalam, J. Karthik, A. R. Damodaran, J. C. Agar, L. W. Martin, Unexpected crystal and domain structure and properties in compositionally graded $PbZr_{1-x}Ti_xO_3$ thin films, *Adv. Mater.* **25**, 1761 (2013).
8. J. Karthik, R. V. K. Mangalam, J. C. Agar, L. W. Martin, Large built-in electric fields due to flexoelectricity in compositionally graded ferroelectric thin films, *Phys. Rev. B* **87**, 024111 (2013).
9. J. Karthik, J. C. Agar, A. R. Damodaran, L. W. Martin, Effect of 90° domain walls and thermal expansion mismatch on the pyroelectric properties of epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ thin films, *Phys. Rev. Lett.* **109**, 257602 (2012).

Program Accomplishments: Presentations

1. J. C. Agar, R. V. K. Mangalam, A. R. Damodaran, G. Velarde, L. W. Martin, *Domain Wall and Intrinsic Contributions to Dielectric Permittivity in Epitaxial $PbZr_{1-x}Ti_xO_3$ Thin Films*, Materials Research Society Spring Meeting (Apr. 2014, San Francisco, CA).
2. L. W. Martin, *New Modalities for and Understanding of Strain Control of Properties in Ferroelectric Thin Films*, Materials Research Society Spring Meeting (Apr. 2014, San Francisco, CA). [Invited]
3. L. W. Martin, *The Science and Engineering of Functional Complex Oxide Thin Films*, Department of Physics Colloquium, Indiana University (Jan. 2014, Bloomington, IN). [Invited]
4. B. Bhatia, H. Cho, J. Karthik, J. Choi, D.G. Cahill, L.W. Martin, and W.P. King, "High Power Density Pyroelectric Energy Conversion using a MEMS Platform," MRS Fall Meeting, Boston, MA, 2013.
5. L. W. Martin, *Strain Version 2.0: Pushing the Edge of Epitaxial Strain Through Compositional Gradients*, Materials Research Society Fall Meeting (Dec. 2013, Boston, MA) [Invited]
6. B. Bhatia, H. Cho, J. Karthik, J. Choi, D.G. Cahill, L.W. Martin, and W.P. King, "Energy Conversion from $BaTiO_3$ Thin Films using the Pyroelectric Ericsson Cycle," ISHMT-ASME Heat and Mass Transfer Conference, IIT Kharagpur, India, 2013. (P K Sarma Award for Best Poster)
7. L. W. Martin, *Flexoelectric Effects in Compositionally Graded Ferroelectric Thin Films – Towards Strain 2.0*, IEEE International Symposium on Applications of Ferroelectrics Meeting (July 2013, Prague, Czech Republic) [Invited]
8. L. W. Martin, *Probing and Controlling Thermal-Electrical Responses in Exotic Ferroelectric Thin Films*, Department of Physics Colloquium, West Virginia University (April 2013, Morgantown, WV) [Invited]
9. L. W. Martin, *Fundamentals of Complex Oxide Thin-Film Growth and Characterization*, Invited Tutorial, American Physical Society March Meeting 2013 (March 2013, Baltimore, MD) [Invited]
10. L. W. Martin, *Domain Structures and Switching in Ferroelectric Thin Films*, 12th International Workshop on Piezoresponse Force Microscopy and Nanoscale Electromechanics: Theory, Techniques, and Applications, Oak Ridge National Laboratory (March 2013, Oak Ridge, TN) [Invited]
11. L. W. Martin, *"Mining" Existing Materials for Useful Functionalities – A Material Maker's Perspective*, National Science Foundation, Materials By Design II Workshop (Feb. 2013, Arlington, VA) [Invited]
12. L. W. Martin, *The Science and Engineering of Thermal-Electrical Responses of Materials*, Department of Materials Science and Engineering Colloquium, University of California, Berkeley (Feb. 2013, Berkeley, CA) [Invited]
13. J. Kardel, Z. Connell, J. Agar, J. Karthik, A. R. Damodarn, L. W. Martin, *Pyroelectric Properties of Epitaxial Ferroelectric Thin Films*, Fundamental Physics of Ferroelectrics and Related Materials 2013 (Jan. 2013, Ames, IA)
14. B. Bhatia, J. Karthik, T. Trong, D. G. Cahill, L. W. Martin, W. P. King, *Pyroelectric Measurements on $PbZr_{0.2}Ti_{0.8}O_3$ Epitaxial Layers*, Materials Research Society, Fall 2012 Meeting, Symposium AA: Oxide Nanoelectronics and Multifunctional Dielectrics (AA19.03) (Nov. 2012, Boston, MA)
15. J. C. Agar, J. Karthik, A. R. Damodaran, V. Mangalam, L. W. Martin, *Dielectric and Electrocaloric Properties of $PbZr_xTi_{1-x}O_3$ Thin Films Near the Morphotrophic Phase Boundary*, Materials Research Society, Fall 2012 Meeting, Symposium AA: Oxide Nanoelectronics and Multifunctional Dielectrics (AA9.31) (Nov. 2012, Boston, MA)
16. L. W. Martin, *Enhanced Thermal-Electrical Responses in Ferroelectric Thin Films*, Département de Physique de la Matière Condensée Colloquium, Université de Genève (March 2012, Geneva, Switzerland) [Invited]
17. L. W. Martin, *Engineering Thermal-Electrical Responses in Complex Oxides: Enhanced Dielectric and Pyroelectric Response in Epitaxially Strained Ferroelectric Thin Films*, Department of Materials Science and Engineering Colloquium, University of Michigan (Jan. 2012, Ann Arbor, MI) [Invited]
18. L. W. Martin, *Engineering Thermal Properties and Response of Epitaxial Oxide Thin Films for Advanced Devices*, Workshop on Oxide Electronics (Sept. 2011, Napa, CA) [Invited]
19. L. W. Martin, *Understanding and Manipulating Defects in Complex Oxide Materials – Implications for Properties and Devices*, HP Labs Colloquium (Sept. 2011, Palo Alto, CA) [Invited]
20. L. W. Martin, *Engineering Thermal-Electrical Responses in Complex Oxides: Enhanced Dielectric and Pyroelectric Response in Epitaxially Strained Ferroelectric Thin Films*, Department of Materials Science and Engineering Colloquium, University of California, Berkeley (Sept. 2011, Berkeley, CA) [Invited]

AFOSR Deliverables Submission Survey

Response ID:3672 Data

1.

1. Report Type

Final Report

Primary Contact E-mail

Contact email if there is a problem with the report.

lwmartin@illinois.edu

Primary Contact Phone Number

Contact phone number if there is a problem with the report

217-244-9162

Organization / Institution name

University of Illinois, Urbana-Champaign

Grant/Contract Title

The full title of the funded effort.

Solid State Cooling with Advanced Oxide Materials

Grant/Contract Number

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-11-1-0073

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Lane Martin

Program Manager

The AFOSR Program Manager currently assigned to the award

Ali Sayir

Reporting Period Start Date

06/01/2011

Reporting Period End Date

05/31/2014

Abstract

This program explored electro-caloric materials for solid state cooling. As part of our work, we aimed to address gaps in the understanding of how to control and exploit these effects for real engineering systems by developing theoretical and experimental approaches to study thermodynamic properties and effects in thin film systems. The Program aimed to overcome these challenges by producing a comprehensive approach that combines design, synthesis, and characterization of thin film oxides (something called for by researchers in the field), a focus on assessing (un)common losses and limiting effects in these materials, and the exploration of new materials and routes to enhance field-induce entropic effects. As part of this, we worked to develop methodologies to directly probe and distill the fundamental response of these materials in operation. In essence we asked the question of how does one produce large field-driven entropic changes in materials. All told, the program combined phenomenological modeling, advanced materials synthesis, and new measurement techniques to understand the fundamental

materials science and engineering of solid state cooling materials. The major discoveries of the program include:

1) The discovery and validation of novel, high-performance cooling materials based on compositionally-graded versions of materials that possess figures of merit of solid state cooling 3-12-times larger than traditional materials. This includes the development of phenomenological models to support this work.

2) The synthesis and study of other candidate high-performance materials possessing strong lattice-polarization coupling and electric-field response. Fundamental insights into how strain and residual strain in materials can be used to deterministically tune the parameters important for electrocaloric cooling were completed.

3) New understanding of intrinsic (arising from temperature-driven changes in polarization), extrinsic (arising from the temperature-dependent motion of domain walls), and secondary (arising from thermal expansion mismatch between the film and the substrate) contributions to thermal response in realistic polydomain films was obtained. This includes the development of the first phenomenological models to include all three effects, measurements aimed a separating the effects, and demonstration of deterministic control of these effects to produce high-performance materials.

4) Identification and quantification of elastocaloric effects in materials. This previously underappreciated potential loss or reduction of performance in these materials was probed by directly measuring both the polarization change with temperature (dP/dT) and the entropy change with temperature (dS/dE). It is observed that both the total pyroelectric and electrocaloric coefficients are not the same and that the difference simplifies to a product of the piezoelectric coefficient, the elastic constant, and the coefficient of thermal expansion. We propose that the piezoelectric effect causes a lattice expansion which subsequently lowers the frequencies of the lattice vibrations and, in turn, increase the vibrational entropy. This effect is called the elastocaloric effect and, in this case, opposes the electrocaloric effect.

5) Development novel, microfabrication-based platforms to characterize the electrocaloric temperature change in nanometer-scale thin films. These microfabricated platforms provides independent control of the out-of-plane electric field across the active electrocaloric film while simultaneously allowing measurement of the resulting temperature change from the corresponding resistance change of the electrically isolated metal strip thermometer. The superimposition of the periodic electric field across the film thickness and sensing voltage along the thermometer strip at different frequencies results in an electrocaloric temperature change at the sum and difference of these two frequencies which is measured using a lock-in amplifier. Based on our measurements on multiple films with varying electrical resistivity we conclude that minimizing the resistive heating in these thin films is critical for electrocaloric refrigeration applications.

The program has run from June 1, 2011 to May 31, 2014 and has supported 2 graduate student researchers (spread across the three PIs). During the duration of the program, we have had three Program Managers. The program was started under Dr. Kumar Jata before being transferred to Dr. Joan Fuller who administered the first year review. From there the program was transferred to Dr. Ali Sayir who has served as the cognizant Program Manager since that time.

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Archival Publications (published) during reporting period:

1. T. Tong, J. Karthik, L. W. Martin, D. G. Cahill, Secondary effects in wide frequency range measurements of the pyroelectric coefficient of Ba0.6Sr0.4TiO3 and PbZr0.2Ti0.8O3 epitaxial layers, in preparation May 2014.
2. R. Xu, J. Zhang, Z.-H. Chen, J. Karthik, L. W. Martin, Orientation dependent structural phase diagrams and dielectric properties of PbZr1-xTixO3 Part I. monodomain thin films, under review at Phys. Rev. B May 2014.
3. T. Tong, J. Karthik, R. V. K. Mangalam, L. W. Martin, D. G. Cahill, Reduction of the electrocaloric entropy change of ferroelectric PbZr1-xTixO3 epitaxial layers due to an elastocaloric effect, under review at Phys. Rev. Lett. May 2014.
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5. J. C. Agar, R. V. K. Mangalam, A. R. Damodaran, G. Velarde, J. Karthik, M. B. Okatan, Z. H. Chen, S. Jesse, N. Balke, S. V. Kalinin, L. W. Martin, Tuning susceptibility via misfit strain in relaxed morphotropic phase boundary PbZr1-xTixO3 epitaxial thin films, Adv. Mater. Interfaces (2014). (DOI: 10.1002/admi.201400098).
6. R. V. K. Mangalam, J. C. Agar, A. R. Damodaran, J. Karthik, L. W. Martin, Improved pyroelectric figures of merit in compositionally graded PbZr1-xTixO3 thin films, ACS Appl. Mater. Interfaces 5, 13235 (2013).
7. R. V. K. Mangalam, J. Karthik, A. R. Damodaran, J. C. Agar, L. W. Martin, Unexpected crystal and domain structure and properties in compositionally graded PbZr1-xTixO3 thin films, Adv. Mater. 25, 1761 (2013).
8. J. Karthik, R. V. K. Mangalam, J. C. Agar, L. W. Martin, Large built-in electric fields due to flexoelectricity in compositionally graded ferroelectric thin films, Phys. Rev. B 87, 024111 (2013).
9. J. Karthik, J. C. Agar, A. R. Damodaran, L. W. Martin, Effect of 90° domain walls and thermal expansion mismatch on the pyroelectric properties of epitaxial PbZr0.2Ti0.8O3 thin films, Phys. Rev. Lett. 109, 257602 (2012).

Changes in research objectives (if any):

N/A

Change in AFOSR Program Manager, if any:

The program has run from June 1, 2011 to May 31, 2014 and has supported 2 graduate student researchers (spread across the three PIs). During the duration of the program, we have had three Program Managers. The program was started under Dr. Kumar Jata before being transferred to Dr. Joan Fuller who administered the first year review. From there the program was transferred to Dr. Ali Sayir who has served as the cognizant Program Manager since that time.

Extensions granted or milestones slipped, if any:

N/A

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
Non-Military Government Personnel Costs			

In-house Contractor Costs			
Travel (Be Specific)			
Training (Be Specific)			
Supplies			
Other Expenses (Be Specific)			
Total Resource Requirements			

Report Document

Appendix Documents

2. Thank You

E-mail user

May 31, 2014 15:35:45 Success: Email Sent to: lwmartin@illinois.edu